Laboratory Manual for General and Inorganic CHEMISTRY

Z. Vasilyeva,
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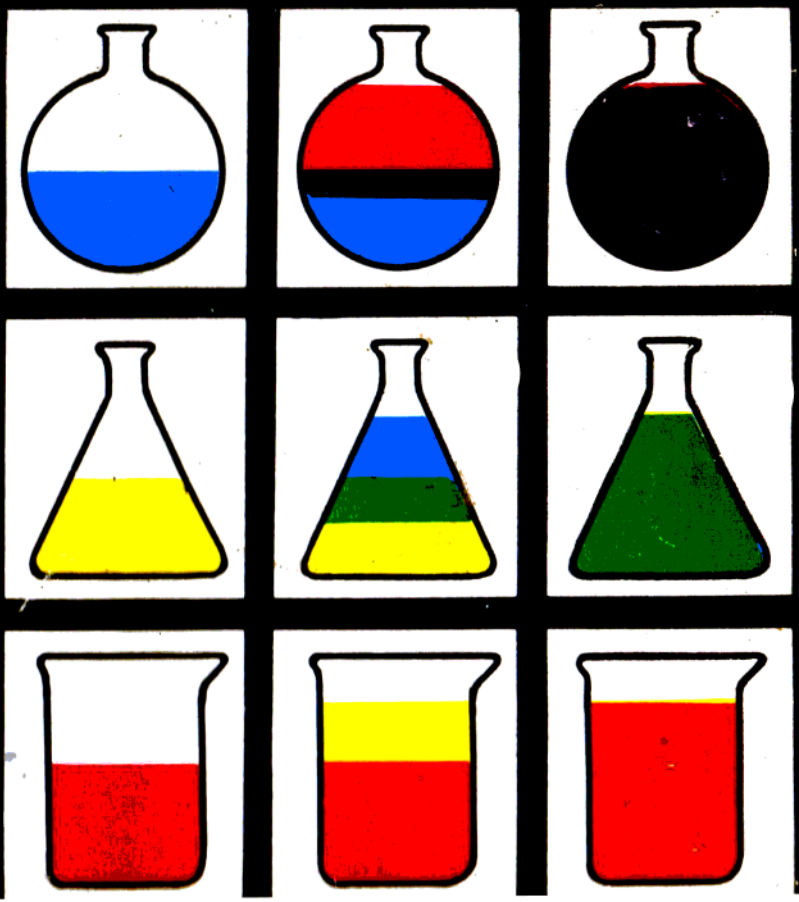

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The book includes fundamental laboratory experiments in general chemistry with reference to atomic theory and thermodynamics. The elements of Mendeleev's periodic table are studied. Each chapter is preceded by review and multiple-choice questions for students and teachers. The use of the semimicro-method allows one to spare valuable reagents and save time. Many chapters are concluded with instructions for the synthesis of inorganic compounds.
Intended for university students not specializing in chemistry.

З. Васильева,
А. Грановская,
А. Таперова

Лабораторные работы по общей
и неорганической ХИМИИ

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Laboratory Manual for General and Inorganic CHEMISTRY

Z. Vasilyeva,
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Preface

This selection of laboratory experiments in general and inorganic chemistry is intended for students preparing themselves for specialities other than chemical. The book is the result of many years of experience the authors acquired in teaching chemistry at the Moscow Institute for Steel and Alloys.

The semimicromethod was developed by the authors, and improvements have been added over the decades. The advantages of this method are quite obvious: dealing with small amounts of reagents trains the student in concentration and accuracy; since only minute quantities are required in the experiments, expensive reagents may be used; conditions in the laboratory are improved with respect to safety; each student is supplied with his own set of the apparatus, reagents and glassware, and thus undue walking about the room is made unnecessary. The latter, in turn, provides an atmosphere of orderliness in the laboratory.

The textbook covers material in all fields of general chemistry and deals with all groups of chemical elements in the periodic table. The experiments are described and interpreted from the point of view of the modern theory of the structure of substances and chemical thermodynamics.

There is no theoretical discussion in this textbook, but the experimental part of each chapter is preceded by questions and problems for independent study before the student proceeds to practical work in the laboratory. A given property or a phenomenon is often demonstrated by several experiments with different substances, and therefore the instructor can choose experiments to meet the special requirements of the curriculum.

Many years have passed since this course in semimicromethod first appeared in print. Each new edition was substantially revised until the book appeared in its present seventh edition which has kept pace with the advances in modern theory and practice in general and inorganic chemistry.

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1 Laboratory Equipment and Safety Rules. Special Features of Semimicromethod

1.1. GENERAL INSTRUCTIONS

From the very start the student should perform laboratory experiments accurately and with attention to detail, otherwise the results may be erroneous and accidents may happen.

The student's main place of work is his bench, which should be kept clean. All objects that are necessary during the experiment should be placed on the bench in a definite order so that they are conveniently at hand and do not hamper manipulations. It will be most convenient to have the test-tube rack and set of reagent bottles in the middle of the bench, the laboratory manual and the log-book on the right, and the burner, ring stand, bath, wash bottle, etc., on the left.

All observations made during work should be recorded after the particular experiment in the student's log-book. Do not make rough notes on odd bits and pieces of paper.

Only pure reagents, clean glassware rinsed with distilled water can be used for experiments. Never take a pipette or a reagent from someone else's bench, since this not only disturbs one's neighbour working but can also contaminate the reagent. Report any missing reagents or laboratory equipment to the laboratory assistant.

Stock reagents should be kept on shelves and should not be transferred to the individual's bench. Laboratory work should be done without undue haste so that reagents are not spilled. If any reagent gets on the bench *it should never be put back into the bottle with pure reagent*, but should be swept and given to the laboratory assistant, and the bench immediately washed and wiped.

Apparatus and reagents must be handled with care. Expensive or poisonous reagents (particularly solutions containing compounds of silver and mercury) should never be discarded into the sink, but should be poured into special bottles intended for the purpose. Waste paper, broken glassware etc. can only be placed in special containers.

Hot glassware should be placed on an asbestos mat.

Special precautions must be taken and safety rules observed in the laboratory. Never work with highly inflammable substances near a

lighted burner. *Poisonous and foul-smelling substances should only be handled in the hood.*

During experiments, reagents of the required concentration and in the recommended amounts should be taken. Never perform any supplementary experiments without the permission of your laboratory instructor.

If large amounts of liquid acid or alkali are spilled, the laboratory assistant should be informed at once and the spilled reagent quickly wiped up with cotton waste taking care not to burn one's hands or damage one's clothes. Concentrated alkali or acid should be handled with special care. If any gets on the skin, the latter should be washed immediately with running water, and first aid obtained from the laboratory assistant.

In all cases of accident inform immediately the laboratory instructor and, if necessary, consult a doctor.

It is prohibited to eat in the laboratory.

1.2. LABORATORY EQUIPMENT

Laboratory apparatus and equipment are of two kinds: that for general use and that for individual use. The first kind includes heating devices (burners, drying cabinets, muffle furnaces), balances, cylinders with liquefied gases, microscopes, pH-meters, vacuum filtration apparatus, etc. They are always present in the laboratory for use by students whenever necessary. Now we shall consider laboratory equipment that is frequently used in experiments, while other apparatuses will be discussed in more detail in the corresponding laboratory experiment.

Heating devices. Gas burners [Teclu burner (Fig. 1) and Bunsen burner (Fig. 2)] and electric stoves are used in the chemical laboratory for heating.

Gas burners. When lighting up a burner or extinguishing the flame, use a tap on the gas mains. *Never extinguish the Teclu burner by means of a gas adjusting screw 6*, for it is only used for fine adjustment of the flame. The air supply is regulated by turning disc *4* on the Teclu burner or air control band *4* on the Bunsen burner.

By changing the air supply, the degree of gas combustion and hence the temperature of the flame can be controlled. If disc *4* is screwed up tight against the chimney, i.e. when the gap is closed and supply of air is cut off, combustion is incomplete and the flame will be luminous and smoky. When the gap is too wide, air supply is increased and the flashback occurs, which either extinguishes the flame or drives it up into the chimney, which becomes overheated. The burner should not be used in either of these cases.

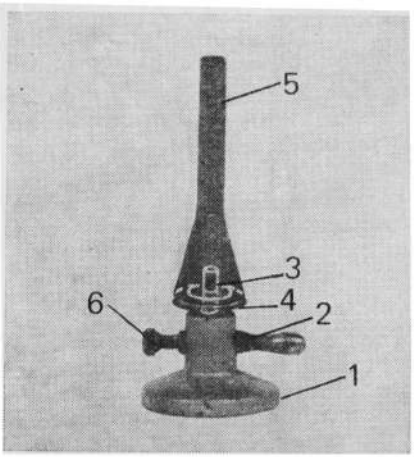


Fig. 1.
Teclu burner:
1–base; *2*–gas inlet;
3–gas nozzle; *4*–adjusting disc controlling intake of air;
5–chimney; *6*–gas adjusting screw

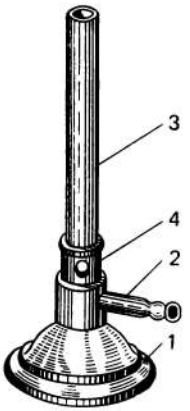


Fig. 2.
Bunsen burner:
1–base; *2*–gas inlet;
3–tube; *4*–air control band

Fig. 3.
Structure of flame

The air adjusting disc should be set so as to ensure sufficient air supply and complete combustion of the gas without noise or soot, and with a steady flame.

A properly adjusted flame is transparent with a bluish tinge, it is non-luminous, and produces no soot. Two zones can easily be distinguished in it (see Fig. 3): an inner zone (shaded in the figure) and an outer zone. The temperature of the inner zone is 300-350°C. Decomposition of the town gas takes place at the lower part *1* of the inner zone, while incomplete combustion of the gas with liberation of free carbon (hot particles of which are responsible for luminosity)

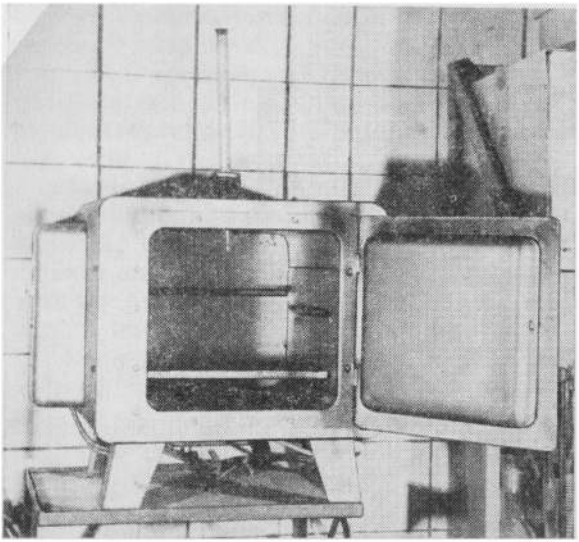


Fig. 4.
Drying cabinet with electrical heating and a thermoregulator

takes place at upper part *2*. This part of the flame is the "reducing" flame since the carbon particles are readily oxidized here and become a reducing agent.

The highest temperature (up to 1500°C) is obtained in the almost colourless upper part *2* of the outer zone, where the gas burns intensively owing to the excess of the air. This part is termed "oxidizing", since substances combine with oxygen in it. Knowing the structure of the flame one can understand that any object being heated should not be lowered deeply into the flame, but should rather be positioned over the upper hottest part of the flame. In this way heating will be most efficient. Oxidizing and reducing properties of the flame will be discussed below in the appropriate experiments.

A burner or electric stove can be used for heating substances in a porcelain dish or crucible. Solutions and crystals in test tubes can also be heated with these devices but only slightly. In this case the test tube should be moved over the flame or the stove in order to ensure uniform heating of its contents. The mouth of the test tube should be directed away from the student or his neighbour in the laboratory. If long heating in a glassware is required, asbestos gauze should be placed on the electric stove or on a ring of the stand.

If a substance is to be heated to temperatures below 100°C, a water bath is used. It is a metal or glass reservoir containing water and provided with an electric heater (or heated over a gas burner).

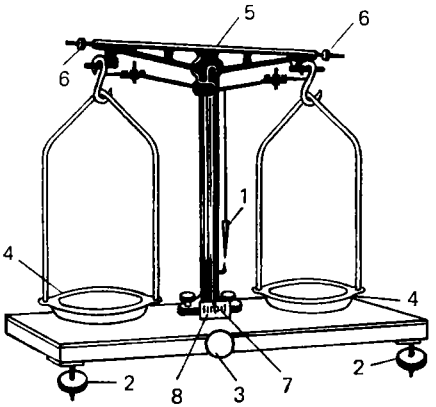


Fig. 5.
Chemical balance:
1–plumb line; *2*–levelling screws; *3*–arrester; *4*–pans; *5*–beam; *6*–adjusting nuts; *7*–pointer; *8*–scale

Drying cabinet (Fig. 4) is an electrically heated apparatus provided with a thermoregulator which maintains the required temperature inside the cabinet. Temperature is measured by means of a thermometer. The substance to be dried is placed in the drying cabinet and kept there at the required temperature for a certain period of time. In quantitative determinations a substance is dried several times until a constant mass is obtained.

Balance and weighing. The accuracy of 0.02 g during weighing is sufficient for most laboratory experiments in general chemistry, and a chemical balance will be found convenient for the purpose.

A chemical balance (Fig. 5) has a base plate provided with adjusting screws *2* used to balance the pans with the help of a plumb line *1*.

The main part of the balance is a post or upright with beam *5* and pans *4*. The beam has three prisms and two adjusting nuts *6*. One prism is located at the middle of the beam with its knife edge resting on the post. The other two prisms are located at the ends of the beam and bear the pans. To prevent wear of the knife edges, the beam and pans are lifted, when not in use, by means of a special device *3* called arrester.

The setting and adjustment of balances is the job of the laboratory assistant.

A box with a set of weights and forceps for picking them up is kept beside the balance.

Weighing rules:

1. Never transfer the balance from one place to another.
2. Handle it with great care and attention.
3. Before weighing anything check the following:

(a) the levelling of the balance (against the plumb line); if its position needs correcting, adjust it by means of the levelling screws;

(b) the equilibrium of the balance, by turning the arrester clockwise and seeing that pointer *7* deviates from zero of scale *8* by the same number of graduations; any imbalance should be eliminated by the laboratory assistant.

4. Never place hot or greasy objects on the pans.

5. Place the weights and substances to be weighed onto the pans, and remove them only when the balance is arrested.

6. Substances to be weighed should be put onto the left-hand pan. Reagents should always be weighed on a watch glass, in a weighing bottle, or on paper.

7. Weights should always be placed on the right-hand pan.

8. Weights should be placed or removed only with forceps and should always be put into the box when not in use.

9. During the experiment, the same balance and the same set of weights should be used. Any object weighing from 0.01 to 211.1 g can be weighed using the following set of weights: 100 g, 50 g, 20 g, 20 g, 10 g, 5 g, 2 g, 2 g, 1 g, and plates 0.5 g, 0.2 g, 0.2 g, 0.1 g, 0.05 g, 0.02 g, 0.02 g, and 0.01 g.

10. When a substance is being weighed, put the heaviest weight to be used onto the pan first, and then add the smaller ones.

11. When weighing is finished, calculate the weight from the empty nests in the box and then check it by adding up the weights on the pan. Remove the weights from the pan and put them into the corresponding nests in the box.

12. Leave the balance clean and in proper order at the end of weighing.

Whenever an accuracy of 0.0002 g is required, an analytical balance should be used.

An *analytical balance* is more accurate and sensitive than a chemical balance. A detailed description of an analytical balance will be found in the relevant instructions supplied together with the balance. Students are permitted to work with an analytical balance only after they become acquainted with the design and instructions.

It should be remembered that the accuracy of calculations should agree with the accuracy of weighing: if substances are weighed to an accuracy of 0.02 g, calculations are carried out to an accuracy of the second decimal.

Desiccator. If a substance or a glassware is to be weighed after calcining or drying in a drying cabinet, it should first be cooled to room temperature. In order to prevent a new absorption of moisture from the air, the substance should be cooled in a special apparatus known as a desiccator (Fig. 6). It is used also for long-term drying and storage of hygroscopic substances. Desiccator is a glass vessel of a complicated structure. A water-absorbing agent (calcined calcium chloride, concentrated sulphuric acid or the like) is put on the bottom of the desiccator. A perforated porcelain plate is placed

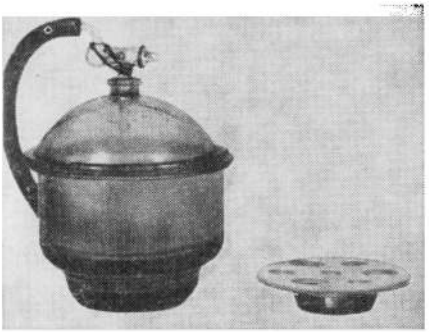


Fig. 6.
Desiccator

inside the desiccator above the conical part, and crucibles, dishes, beakers, etc., containing the substances to be dried or cooled, are put into the holes of the plate. The edges and the lid of the desiccator are ground and coated with vaseline to ensure a tight fit. The lid is put over with a sliding movement and removed in the same way.

Hot objects and apparatuses are handled by means of forceps, crucible tongs or surgical forceps (Fig. 7).

Apparatus for vacuum filtration (Fig. 8) is used for separation of large amounts of solutions from precipitates (in the synthesis, recrystallization) and also to accelerate filtration. The apparatus consists of a thick-walled tapered flask *1* with a tubule (Bunsen flask). The neck of the flask is closed tightly with a rubber stopper provided with a porcelain Büchner funnel *2*. The flat bottom of the funnel is

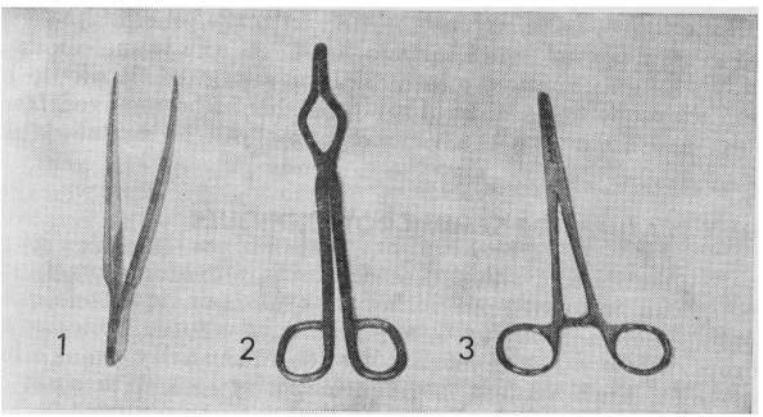


Fig. 7.
Forceps (1); Crucible tongs (2); Surgical forceps (3)

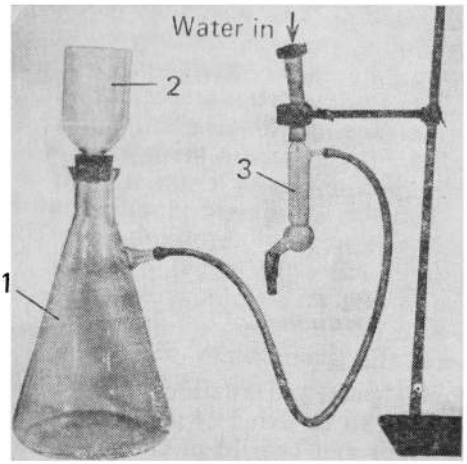


Fig. 8.
Apparatus for vacuum filtration:
1 – Bunsen flask;
2 – Büchner funnel;
3 – water-jet pump

perforated. The flask is connected by a thin rubber tube to a source of vacuum (a vacuum pump, either a mechanical or a water-jet pump *3*). The upper end of the water-jet pump is connected to a tap. When a strong water jet passes through the narrow inner tube, it sucks in air and creates a vacuum in the Bunsen flask. A piece of filter paper is placed on the bottom of the Büchner funnel. The diameter of the paper should be slightly smaller than that of the bottom but large enough to cover the perforations. The filter is wetted with water and a vacuum pump is switched on: the wet filter is "sucked" tightly to the funnel bottom. The solution with the precipitate to be separated is now poured in a continuous jet into the funnel along a glass rod. As soon as the precipitate has been separated, it should be washed on the same filter, the rubber tube should be removed from the tubule, and only then the vacuum pump can be switched off.

1.3. SOME FEATURES OF SEMIMICROTECHNIQUES

Very small quantities of substances are used in semimicromethod. Experiments can be carried out with either solids or liquids. Liquid substances and solutions are used in quantities measured from two to fifteen drops, while a few crystals of solids are usually enough for the experiment. Each student is given a special rack with a set of reagents, glassware, and other facilities that may be required in his work.

Small test tubes are used in the semimicromethod for the storage of reagents.

Fig. 9.
Test tube with a microspatula for dry reagents

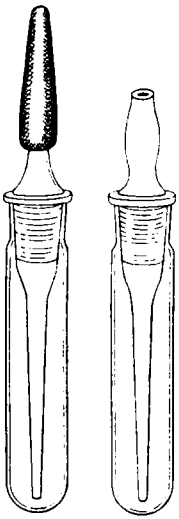


Fig. 10.
Test tubes with ground-in pipettes

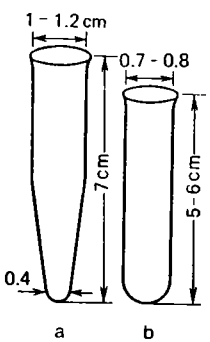


Fig. 11.
Test tubes:
(a) conical; (b) cylindrical

Dry reagents are kept in 3-4 ml test tubes, which are 45-50 mm high and have a diameter of 7-10 mm. The test tubes are fitted with rubber or cork stoppers provided with a microspatula (Fig. 9). The microspatula should be freely movable in the stopper boring. The length of the microspatula is 78-80 mm, the area of its blade is 12-15 mm^2 and the thickness of the blade is not more than 1 mm.

In racks reagents should be kept in 10-12 ml test tubes (Fig. 10) with the inner diameter of 13-15 mm and 90 mm high. The test tubes are provided with dropping pipettes with ground joints. Volatile and hygroscopic substances should be kept in test tubes with ground-

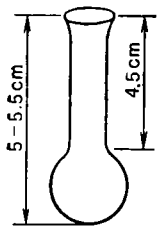


Fig. 12.
Microflask

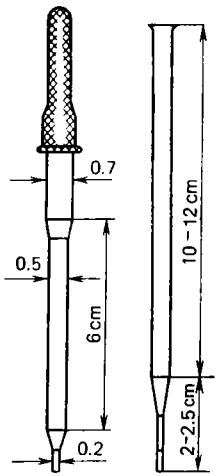


Fig. 13.
Capillary pipettes

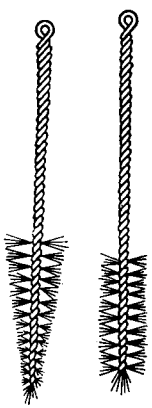


Fig. 14.
Bottle brushes

glass pipettes fitted with rubber bulbs. If ground-glass pipettes are not available, they can be replaced by common rubber stoppers provided with pipettes.

Test tubes containing reagents should have a label with the name of the reagent or its formula. To protect the labels from damage they may be coated with wax.

Each rack is provided with a set of test tubes intended for carrying out experiments: conical test tubes of 5-6 ml volume (Fig. 11*a*) and cylindrical test tubes with a capacity of 2.5-3 ml (Fig. 11*b*). Unless otherwise stated, conical test tubes should be used for carrying out

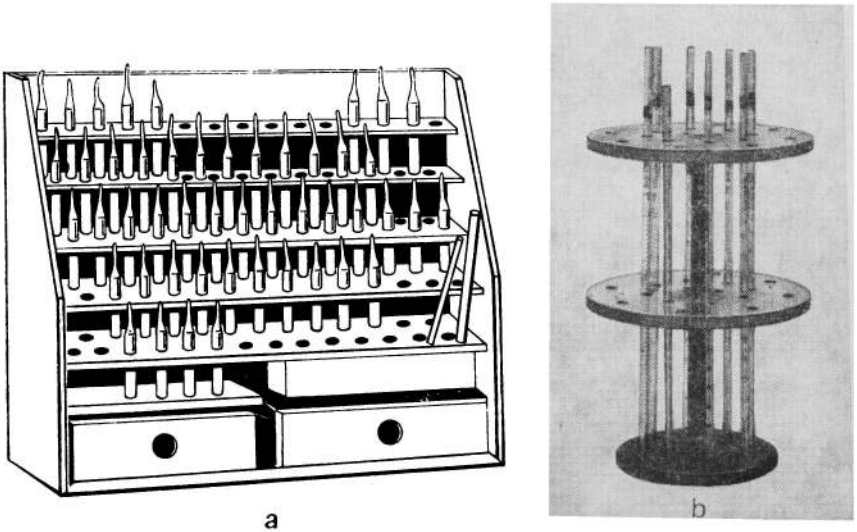


Fig. 15.
Racks for reagents and accessories:
a–open cupboard;
b–a set of disk shelves

experiments. Cylindrical test tubes are best suitable for heating solids.

In addition the rack contains a microflask with a bulb capacity of one millilitre (Fig. 12); a small porcelain crucible (No. 1 or 2); an evaporating dish, 30-50 mm in diameter; watch glass, 25-30 mm in diameter, capillary pipettes, 100-120 mm long and 3-4 mm in diameter, with 20-25 mm long drawn ends (Fig. 13); glass rods, 100-120 mm long, 3 mm in diameter with fused ends, one of which is fitted with a piece of a rubber tube (a policeman); glass slides 20 × 60 mm, 1-2 mm thick (a common slide and with a depression); bottle brushes for washing glassware (Fig. 14); filter paper and an asbestos mat (70 × 70 mm).

There are two types of racks intended to hold the mentioned glassware and accessories for individual use by a student. The first one looks like an open cupboard, 450 mm long, 400-430 mm high, and 220 mm deep (Fig. 15*a*). It is provided with stepped shelves.

The second type (Fig. 15*b*) is a set of disc shelves with the same diameter and arranged one beneath the other. The discs may turn around the vertical axis upon which they are assembled. Racks of the first type have drawers at the bottom (40-45 mm high) to

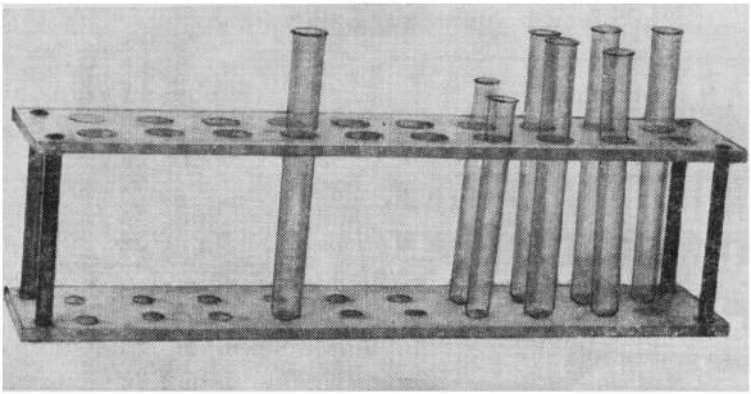


Fig. 16.
Test-tube stand

hold the accessories required for assembling semimicroapparatus. The racks may be plywood or heat-resistant plastic.

Test tubes containing dry reagents should be kept on the lower shelf of the cupboard-type rack and on the upper disc of the round rack. The test tubes intended for carrying out experiments should be kept on the lower shelves in the rack. The second (from the bottom) shelf is intended for distilled water, acids, alkalies, litmus and other indicator solutions. The third and the fourth shelves are intended for all other reagents that may be needed during a particular experiment.

If many test tubes are needed for the experiment, the student should obtain another small test-tube stand (Fig. 16).

Each student should have a wash bottle, a basin, and if necessary, a metal stand.

A **wash bottle** (Fig. 17) is used to wash test tubes during the experiments. 300-500-ml flask with a stopper fitted with two glass tubes can be used for the purpose. One of them is bent at an acute angle and has one end drawn off in a capillary tip; the other end reaches almost to the bottom of the flask. (The drawn capillary end should preferably be connected to the tube with a thin rubber tubing.) The upper end of the other tube is bent at an obtuse angle and the lower end extends 1-2 cm below the stopper. Air is blown into the flask through the shorter tube while water under pressure runs out from the flask through the longer tube.

A **basin**, a crystallizer or some other vessel may be used for spent solutions and washings.

A **metal ring stand** (Fig. 18) is used to fasten pieces of equipment when the experiment proceeds for a long time. The ring stand differs

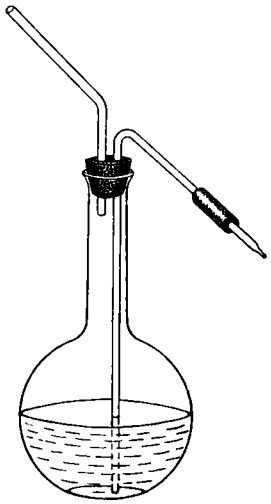


Fig. 17.
Wash bottle

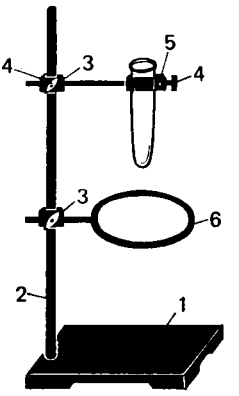


Fig. 18.
Metal ring stand:
1–base; *2*–upright; *3*–couplings; *4*–fixing screws; *5*–clamp; *6*–ring

from the ordinary Bunsen stand by the size and the method of fixation of the ring and the clamp. The stand consists of base *1*, upright *2* (250-300 mm high and 4-5 mm in diameter), and two rectangular couplings *3*. The longer side of the coupling is 40 mm. Each coupling has two 5-6 mm borings, which are mutually perpendicular and spaced at a distance of 20-30 mm from one another. One boring is intended to fasten the coupling, while the other to fix clamp *5* or ring *6*.

An object (a test tube or a flask) is fixed in the clamp with screw *4*. The rod is also fixed in the coupling with screw *4*. By turning the rod inside the boring of the coupling, the object can be fixed in any position (horizontal, vertical, or inclined) that may be required. Ring *6* is 30-35 mm in diameter; the rod is 20-25 mm long.

Water bath. When a substance needs to be heated for a long time at temperatures not exceeding 100°C, or a solution is to be heated at constant temperature, a water bath is used. A bath is also used to heat test tubes containing concentrated acids or alkalies. In most procedures described in this manual a 100-ml beaker is used as a water bath. The beaker is filled with water to two-thirds of its capacity, placed on an asbestos-centred gauze on the ring of the stand, and heated with a gas burner or on an electric plate with a rheostat. Test tubes with reagents are put into hot or boiling water. If a test tube is to be heated for a long time, it is fastened in the clamp of the stand.

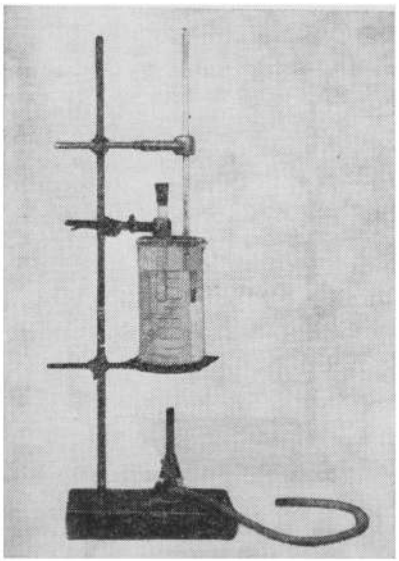


Fig. 19.
Water bath (thermostat)

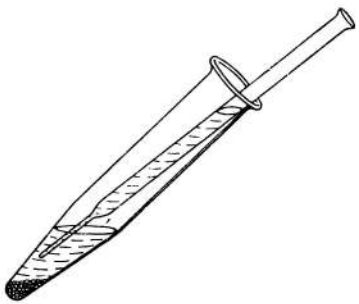


Fig. 20.
Separation of liquid from precipitate after settling

When a water bath is used as a thermostat, a 200-ml beaker is taken and capillaries (sealed at one end) are placed on the bottom to prevent uneven boiling. The beaker is filled with water to three-quaters of its capacity and covered with a metal or wooden lid with holes for test tubes and a thermometer (Fig. 19). Water is heated to the required temperature and the flame adjusted so as to keep the water temperature constant (deviation in the thermometer reading should not exceed $\pm 0.5°C$).

Some useful hints. When a solid substance is transferred to a test tube, the microspatula should be held over the test-tube mouth and should not be lowered inside the test tube. As soon as the required amount of a substance has been transferred into the test tube, the microspatula should be put into the reagent test tube where it belongs. Never use the same spatula to handle different substances.

In order to prevent contamination of reagents, never put the capillary tip of the pipette into the test tube or touch its walls.

A precipitate is usually separated from the liquid phase by settling. When the solution over the precipitate becomes transparent, it is removed with a pipette as shown in Fig. 20. The pipette tip can be wrapped in clean cotton wool.

Certain reactions can be carried out on a slide or porcelain plate. To do this, 1-2 drops of each reagent are placed onto the plate or

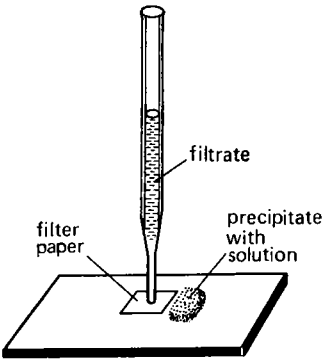


Fig. 21.
Separation of solution from precipitate on a glass or porcelain plate

slide 5-10 mm apart from one another, and the liquids are then mixed with a glass rod. The second reagent can be dropped directly over the first one on the slide.

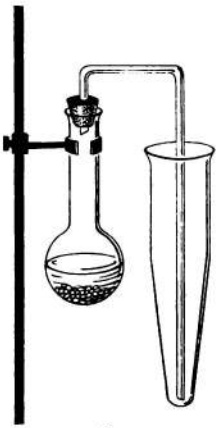
In order to remove the solution from a precipitate obtained on a slide or a porcelain plate, place a piece of filter paper on the slide (or plate) near the mixture. (The filter paper should be folded in four and wetted with water.) A capillary (with a well fused tip) should be pressed tightly to the filter paper and the latter moved to contact with the liquid. The latter is slowly sucked off (Fig. 21). The filtrate in the pipette is transferred into a clean test tube for use in subsequent experiments.

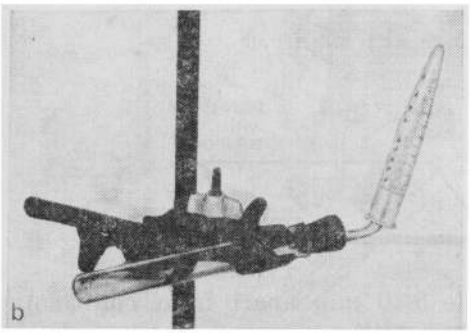
Work with gases. Experiments in which gases are obtained and examined are carried out in apparatuses assembled from test tubes, microflasks, and bent glass tubes interconnected by thin rubber tubes. A microflask is usually used as a reaction vessel. (Test tubes are also used in certain experiments.) The method by which a gas can be collected depends on the properties of a particular gas and the purpose of the experiment. Figure 22 shows typical apparatuses that can be assembled by a student during work with gaseous substances.

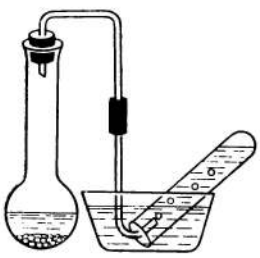
If a gas is produced during heating, the end of the gas-discharge tube should immediately be removed from the basin as soon as the receptacle has been filled with the gas (Fig. 22*c*) or from the liquid when it is not necessary to saturate it with the gas any longer (Fig. 22*d*); otherwise water can be drawn into the reaction vessel as it cools down.

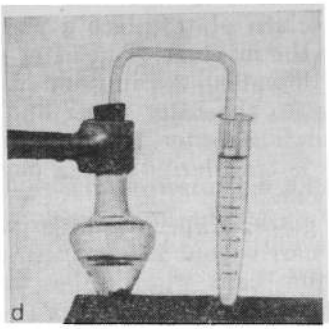
If it is required to establish the colour or smell the odour of the evolving gas, or to observe its burning, it is not necessary to collect the gas in a separate vessel: its colour is obvious to the eye through the glass, while the odour can be smelt by wafting the gas toward the nose.

If the gas should be kept for a time, the test tube should be closed with a well-fitted stopper. Rubber stoppers Nos. 12 and 10 are used









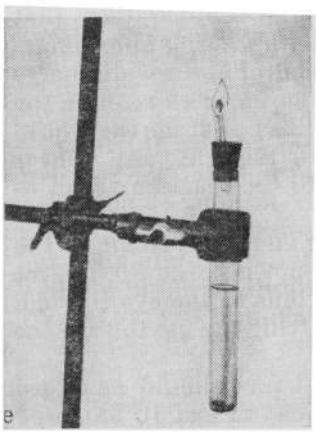


Fig. 22.
Apparatuses for work with gases:
a – apparatus for preparing gas heavier than air
b – apparatus for preparing gas lighter than air
c – apparatus for preparing and collecting gas under water
d – apparatus for absorbing gas by liquid
e – apparatus for combustion of gas in air

for conical test tubes; pieces of rubber tube (7-8 mm long a... 5 mm in diameter) with a glass rod inside them are used instead of stoppers to close cylindrical test tubes.

If the gas is to be tested for combustibility in the air, it is ignited at the outlet of the tube (Fig. 22*e*). It must be remembered, however, that if the gas forms an explosive mixture with air, ignite it 5-10 s after the evolution of the gas has started. This time is sufficient to displace all the air from the apparatus.

Whenever necessary, the evolving gas is purified and dried in wash bottles filled with water or solutions of suitable absorbing and dehydrating agents. The bottles should be installed between the reaction test tube and the gas receptacle.

Washing utensils and glassware. Before the experiment clean glassware should be rinsed with distilled water over a basin and dried, if necessary. Upon termination of the experiment, the glassware and apparatuses should be washed thoroughly.

Any dirt or contaminants should be removed using a brush or a glass rod with a rubber tip (a policeman). Soiled capillaries, glass tubes, test tubes, crucibles and other utensils that cannot be washed with water should be placed in a beaker filled with hydrochloric or nitric acid (which is kept in the hood). After the utensils have been cleaned completely, the acid is poured off carefully into a special beaker for waste acid, while the utensils in the beaker should be rinsed several times with tap water. The clean objects may then be removed from the beaker and rinsed finally with distilled water.

When the laboratory work is over, it is necessary to check that the gas tap is turned off, the reagent rack is in proper order, and the bench is clean. All accessories obtained for the experiment from the laboratory assistant should be handled back.

2 Purification of Substances. Conversions of Chemical Compounds

EXPERIMENT 1. PURIFICATION OF SUBSTANCES

Apparatus and reagents

Drying cabinet.
Liebig condenser. Wurtz flask.
Funnel for filtration of hot solutions.
Büchner funnel. Water-jet pump.
Water bath.
Beakers, 500-ml, 300-ml, and 50-ml. Glass funnels. Flask, 200-300-ml. Round-bottomed flask, 100-200-ml. Measuring cylinder, 50-100-ml. Weighing bottle.
Porcelain dish.
Two watch glasses. Capillary tubes.
Glass rods. Scissors. Soda lime tube.
Asbestos-centred gauze. Filters.
Filter paper. Chemical balance with a set of weights.

Potassium permanganate. Crystalline iodine. Potassium dichromate. Sodium chloride. Chalk.	Solutions: nitric acid, 2 *N*; hydrochloric acid, density 1.19 g/cm^3; barium chloride, 2 *N*.

The methods used for purification of substances are quite varied and depend on the properties of a particular substance and its use. The most common purification methods are filtration, distillation, sublimation, recrystallization, and salting out. Gases are usually purified by absorbing their impurities with substances reacting with these impurities. A pure substance is characterized by specific physical and chemical properties. Consequently, a substance can be tested for purity by the appropriate physical and chemical methods. The physical methods imply the determination of density of a substance, its melting point, boiling point, and other constants. The chemical methods are based on chemical reactions which are used in qualitative and quantitative analysis of substances.

1. Purification of Water from Mechanical Impurities by Filtration and Distillation

Procedure. Pour 400-500 ml of tap water into a beaker and add 2-3 g of crushed chalk. Stir the mixture using a glass rod and prepare a fluted filter to fit the funnel: take a round piece of filter paper, fold it in half and then fold it several times along the radius (with alternation of the folding direction). Cut the edge of the filter so that it is 3-5 mm lower than the edge of the funnel. Place the obtained fluted cone in a glass funnel. Put the glass funnel in the ring of the stand. Place an empty beaker under the funnel so that the funnel end touches the beaker wall and is 2-3 cm lower than the edge of the beaker. Pour the mixture carefully into the filter along a glass rod seeing to it that the liquid level is 4-5 mm lower than the edge of the filter paper (Fig. 23). Add 3-4 crystals of potassium permanganate to the filtrate in order to oxidize organic substances that may be present in it. Transfer the filtrate into a Wurtz flask, drop several capillaries (to prevent vigorous boiling), close the flask with a stopper fitted with a thermometer, and fix the flask in the clamp of the stand on an asbestos-centred gauze (Fig. 24). Connect the tubule of the Wurtz flask with a Liebig condenser which is connected to the tap of water mains. Attach the adapter to the outlet of the condenser and lower it into a receptacle. Fill the condenser with water and adjust the flow rate (not high). Heat the water in the flask to boiling and obtain 200-300 ml of distillate. Stop heating.

In order to remove dissolved gases, boil the obtained water for 10-15 minutes. Close the flask with a stopper with a soda lime tube and allow it to cool. As soon as the water cools to room temperature, close the flask with a tightly fitting stopper. Compare the purity of

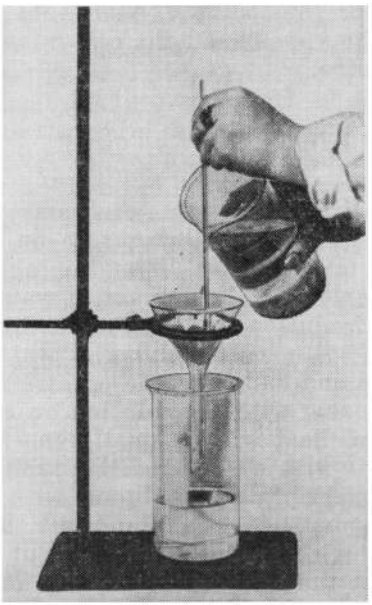


Fig. 23.
Filtration under atmospheric pressure

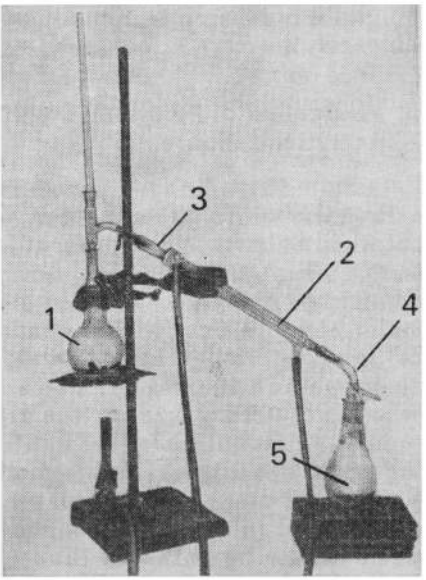


Fig. 24.
Apparatus for distillation of water:
1–round-bottom flask;
2–Liebiq condenser; *3*–adaptor;
4–air-cooled adaptor;
5–receptacle

the distillate with that of tap water. To that end, place 1-ml portions of the distillate and tap water on two separate watch glasses and evaporate to dryness on a water bath. Draw a sketch of the apparatus.

2. Purification of Iodine by Sublimation

(*Use the Hood*!)

Procedure. Using a chemical balance weigh out about 0.3 g of iodine on a watch glass and transfer it into a beaker without a spout. Place the beaker on an asbestos-centred gauze on the ring of the stand. Place a round-bottomed flask filled with cold water on the beaker to cover it tightly. Heat the beaker carefully with a small flame of a burner so that the water in the flask remains cold. Observe the precipitation of iodine vapour in the form of crystals on the cold surface of the flask. As soon as the sublimation is over, cool the flask,

take a piece of filter paper to transfer the iodine crystals into a weighing bottle. Note the colour of the vapour and the colour and shape of the crystals of sublimed iodine.

3. Purification of Potassium Dichromate by Recrystallization

Potassium sulphate is a common impurity in potassium dichromate.

Procedure. Weigh out about 6 g of potassium dichromate on a chemical balance and transfer it into a 50-ml beaker. Using the table of solubility (see Appendix, Table 5) calculate the amount of water required to prepare a saturated at 100°C solution of potassium dichromate. Measure out (with a graduated cylinder) a volume of water 2-3 ml greater than the calculated one and add it to the potassium dichromate in the beaker. Place the beaker with the solution on an asbestos-centred gauze on the ring and heat with a small flame to complete dissolution of the salt. Stir it with a glass rod. Prepare a funnel for hot filtration: place a filter paper into a glass funnel with a wide, short stern, wet the paper with distilled water, and put the glass funnel into a metal cone of the device for hot filtration. Put a clean beaker beneath the funnel. Heat the solution to boiling and filter it hot, pouring small portions along a glass rod. Keep the first solution hot (on the gauze). Cool the filtrate to room temperature with constantly stirring it. Then place the beaker into cold water and observe the precipitation of the crystals. Transfer the recrystallized salt (together with the solution) into the Büchner funnel and separate the obtained crystals. When filtration is over, remove the filter with the crystals and dry them thoroughly with filter paper.

Dissolve a few crystals of the obtained salt in water. Test the mother solution and the solution of recrystallized potassium dichromate for the presence of potassium sulphate. To that end, place 3-5 drops of each solution into separate test tubes and add 1-2 drops of a 2 *N* nitric acid and of barium chloride solutions. Compare the results. Describe the work done in the log-book. Write down your calculations and draw a sketch of the apparatus. Hand over the obtained salt to the laboratory assistant.

4. Purification of Sodium Chloride by Salting Out

The salting-out method is used to recrystallize substances whose solubility changes but little with temperature. Reagents that lower the solubility of such substances are added to their solutions.

Procedure. Prepare a saturated solution of sodium chloride. Weigh out 40 g of table salt on a chemical balance, crush it in a mortar, and transfer into a beaker. Add 100 ml of distilled water and place

the beaker with the solution on an asbestos-centred gauze. Heat the solution to boiling. Filter the solution through a fluted filter into a clean beaker. Measure out 50 ml of concentrated hydrochloric acid (density 1.19 g/cm^3) with a graduated cylinder. Place the beaker with the warm saturated solution of table salt into the hood and add slowly, in small portions, concentrated hydrochloric acid with stirring. When the solution is cooled to room temperature, separate the precipitated crystals on the Büchner funnel, transfer them into a porcelain dish, and dry in a drying cabinet at 110°C. Describe your experiment. Note the decrease in the solubility of sodium chloride after addition of concentrated hydrochloric acid. Will the solubility of sodium chloride decrease if gaseous hydrogen chloride is passed through a saturated sodium chloride solution?

EXPERIMENT 2. PREPARING COPPER FROM COPPER SULPHATE BY CONSECUTIVE CHEMICAL CONVERSIONS

Apparatus and reagents

Apparatus for reduction of copper oxide with hydrogen. Water-jet pump and the Büchner funnel. Beaker, 200-250-ml. Porcelain crucible. Copper sulphate, anhydrous. Zinc granules. Solutions: sodium hydroxide, 1 *N*; hydrochloric acid, 4 *N*.

Procedure. This work is a series of chemical reactions by which copper metal can be prepared from anhydrous copper sulphate in laboratory conditions. Methods and techniques commonly used in laboratory practice are described.

Conversion of anhydrous copper(II) sulphate into a crystal hydrate (blue vitriol). Obtain about 3 g of anhydrous copper(II) sulphate from the laboratory assistant and place it in a dry 200-250-ml beaker. Note the colour of the salt. Pour 100 ml of distilled water into a graduated cylinder. Add a few drops of distilled water to the salt and see how the colour of the salt changes. What is the formula of the obtained crystal hydrate (blue vitriol)?

Preparing copper(II) sulphate solution. Once we know that the anhydrous salt readily converts into a crystal hydrate, add the remaining distilled water to the salt in the beaker and stir the contents with a glass rod until the salt dissolves completely. The prepared solution may contain a small amount of undissolved crystals or mechanical impurities (if commercial copper(II) sulphate is used). The solution should therefore be filtered. Since only solution will be used in subsequent procedure, a fluted filter should be used for rapid filtration.

Precipitation of copper(II) hydroxide. Pour 40 ml of a 1 *N* sodium hydroxide solution into the beaker containing the filtered copper(II) sulphate along a glass rod. Note the colour of the precipitated copper(II) hydroxide. Stir the beaker contents using a glass rod and allow the precipitate to settle.

Preparing copper(II) oxide. In 8-10 minutes, when the main part of copper(II) hydroxide has settled, pour out 3/4 of solution and heat the remaining solution with the precipitate to boiling, stirring the mixture with a glass rod. Note the colour change in the lower layer of the precipitate. Continue heating with a small flame with stirring until complete conversion of copper(II) hydroxide into copper(II) oxide occurs. Control the process by the colour change of the precipitate.

Separating copper(II) oxide from solution by vacuum filtration and washing the precipitate by decantation. As soon as the entire precipitate is black, remove the beaker from the ring and allow to stand. Meanwhile prepare an apparatus for vacuum filtration (see Fig. 8).

Pour the settled solution from the beaker along a glass rod into the Büchner funnel taking care not to stir up the precipitated copper(II) oxide. When the entire solution has been transferred into the Büchner funnel, wash the precipitate in the beaker 2-3 times by decantation. To do so, add 5-8 ml of distilled water to the precipitate in the beaker, stir the mixture using a glass rod and allow the precipitate to settle for 2-3 minutes. Pour the washings carefully into the Büchner funnel along the rod, without stirring the precipitate. This operation is known as decantation. During the third washing, stir the precipitate and transfer it together with the washings onto the filter. Now disconnect the Bunsen flask from the pump by pulling off the rubber tube from the Bunsen flask tubule. Switch off the pump.

Calcining copper(II) oxide. Dry thoroughly the separated precipitate between filter paper sheets and transfer into a porcelain crucible using a spatula. Place a clay triangle on the ring stand and put the crucible containing the precipitate on the triangle. Heat the crucible over a small flame being careful to avoid vigorous spattering of the wet precipitate. As soon as the moisture stops evaporating, calcine the precipitate for 5-10 minutes over a strong flame of the burner. Extinguish the flame and allow the crucible to cool.

Obtaining copper by reducing its oxide with hydrogen. Place a thin layer of the cold oxide into a bent glass tube *1* (the inner diameter, 6-8 mm) fitted with a rubber stopper *2* (Fig. 25). Fasten a 100-150-ml flask in the clamp of the stand and pour 30-40 ml of a 4 *N* hydrochloric acid solution into it. Add 2-3 grains of zinc and close the flask with the stopper fitted with the tube containing copper oxide. Pass hydrogen for 3-4 minutes at room temperature to displace all air from the apparatus. Now carefully (to prevent explosion) heat

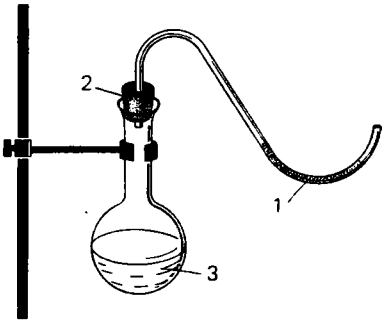


Fig. 25.
Apparatus for reduction of copper oxide:
1–bent tube; *2*–stopper; *3*–flask

the tube containing the oxide with a small flame of the burner. How does the colour of the oxide change? Explain your observations.

Recording the results. Write down the formulas for the chemical compounds that were obtained in the experiment, beginning with anhydrous copper sulphate to copper metal. Write down the equations for the corresponding reactions. Describe the techniques that were used for the first time during this laboratory work.

3 Atomic Theory

QUESTIONS AND PROBLEMS

1. Determine: (a) the number of moles of magnesium contained in 0.486 g of magnesium; (b) the number of moles of aluminium sulphate in 34.2 g of this substance; (c) the number of moles of water in 1 litre of water at 4°C and 760 mm Hg.
Answer: (a) 0.02 mole; (b) 0.1 mole; (c) 55.6 moles.
2. Express in moles and grams the following: (a) 6.02×10^{21} molecules of acetylene C_2H_2; (b) 2.00×10^{23} molecules of phosgene $COCl_2$.
Answer: (a) 0.01 mole, 0.26 g; (b) 1/3 mole, 33 g.
3. Decide if the following quantities contain equal number of molecules: (a) 1 g of hydrogen and 1 g of oxygen; (b) 1 mole of hydrogen and 1 mole of oxygen.
4. Write down the simplest and a true chemical formula of a gas of the following composition: 82.76% C, 17.24% H. The density of the gas with respect to air is 2.01.
5. As 2.94 g of calcium chloride crystal hydrate were calcined, 1.45 g of water was liberated. Write down the formula of the crystal hydrate.
6. What volume will 1 kg of a gas mixture occupy at 0°C and 760 mm Hg if the composition of the gas mixture is the following: (a) NO 20%, N_2 40% and CO_2 40%; (b) C_2H_2 20%, CH_4 40% and CO 40%.
Answer: (a) 673 l; (b) 1052 l.
7. Determine the molecular weight of gases if: (a) 0.29 l of a gas at 27°C and 800 mm Hg weighs 0.32 g; (b) 1.56 l of a gas at 27°C and 780 mm Hg weighs 2.86 g.
Answer: (a) 25.6; (b) 44.

8. The density of gases with respect to air is (a) 0.9 and (b) 2.45. Determine the weight of 1 litre of each gas.
Answer: (a) 1.16 g; (b) 3.17 g.
9. How many atoms do the molecules of the following substances contain: (a) sulphur vapour at 950°C, if its density with respect to air is 2.2; (b) antimony vapour at 2000°C, if its density with respect to hydrogen is 60.88?
10. When a sample of lead(II) nitrate was calcined, its weight decreased by 2.16 g. Determine the weight in grams, the number of moles of the salt, and also the volumes of the obtained oxygen and nitrogen dioxide at STP.
Answer: $Pb(NO_3)_2$—6.62 g; 0.02 mole; $V_{O_2} = 0.224$ l; $V_{NO_2} = 0.448$ l.
11. What quantity (in grams) of calcium carbonate should be decomposed to prepare carbon dioxide in amount sufficient to fill a 40-litre cylinder at 15°C and 760 mm Hg (10 atm)?
Answer: 1690 g.
12. What volume of oxygen at 300°C and 3800 mm Hg (5 atm) will be consumed during burning of 10 kg of coal to obtain CO_2, if the carbon content is 94%? What volume will this carbon dioxide occupy under the same conditions?
Answer: 7.36 m^3.
13. Determine the content of calcium carbonate (in per cent) in limestone, if calcination of 1 g of limestone gives 0.225 l of carbon dioxide at 0°C and 680 mm Hg. Assume that the limestone contains no other carbonates.
Answer: 89.7%.
14. Calculate equivalent weights for the following elements: (a) tin, if heating of 0.92 g of tin in a stream of oxygen gives 1.17 g of tin oxide; (b) tin, if reduction of 1.17 g of tin oxide with hydrogen gives 0.16 g of water; (c) magnesium, if during its heating in a stream of oxygen its weight increased by 66.7%; (d) manganese, if during reduction of 2.17 g of manganese oxide with aluminium, 1.7 g of Al_2O_3 was formed.
Answer: (a) 29.7 g; (b) 59.3 g; (c) 12.0 g; (d) 13.7 g.
15. 1 g of potassium combines with 0.9 g of chlorine and 2.0 g of bromine. Determine equivalent weights of potassium and bromine, if the equivalent weight of chlorine is 35.5 g.
Answer: 39 g; 78 g.
16. What quantity in grams of oxide will be obtained by oxydizing 3 g of a metal whose equivalent weight is 9 g?
Answer: 5.7 g.
17. Write down the formula of a compound of antimony with (a) sulphur; (b) oxygen, if the atomic weight of antimony is 121.8 and its equivalent weight is 40.6 g, while the atomic weight of sulphur is 32 and the equivalent weight is 16.
18. Determine equivalent weights of acids and bases in the following reactions:

(a) $HNO_3 + Bi(OH)_3 = Bi(OH)_2NO_3 + H_2O$
(b) $H_2S + NaOH = NaHS + H_2O$
(c) $3H_2SO_4 + 2Al(OH)_3 = Al_2(SO_4)_3 + 6H_2O$
(d) $H_3PO_4 + Ca(OH)_2 = CaHPO_4 + 2H_2O$
(e) $2HCl + Bi(OH)_3 = BiOHCl_2 + 2H_2O$
(f) $3Ca(OH)_2 + 2H_3PO_4 = Ca_3(PO_4)_2 + 6H_2O$

19. What volumes will an equivalent weight of oxygen and an equivalent weight of hydrogen occupy at STP?
Answer: $V_{O_2} = 5.6$ l; $V_{H_2} = 11.2$ l.
20. Determine the equivalent weight of a metal if 0.046 g of the metal displace 62.35 ml of hydrogen from an acid. Hydrogen is collected above water at 17°C and 764.5 mm Hg. Water vapour pressure at 17°C is 145.3 mm Hg.
Answer: 88.9 g.
21. Determine the equivalent weight of a metal if its 0.0350 g (containing

20 per cent impurities which do not react with the acid) displaces 11.9 ml of hydrogen collected above water at 17°C and a pressure of 145.3 mm Hg. Water vapour pressure at 17°C is 774.5 mm Hg.
Answer: 28 g.
22. Determine percentage content of impurities in commercial iron sulphide, if 0.8 l of hydrogen sulphide is liberated during the reaction of 5 g of the salt with an acid at 39°C and 1216 mm Hg.
Answer: 12 per cent.
23. 20 kg of commercial calcium oxide were roasted in an electric furnace to give 16 kg of calcium carbide. The reaction equation is: $CaO + 3C = CaC_2 + CO$.
Determine the percentage content of impurities in calcium oxide and the theoretical volume of carbon monoxide at 546°C and 760 mm Hg.
Answer: 30 per cent of impurities; $V_{CO} = 16.8$ m³.

Examples of Multiple-choice Questions

1. How many molecules does 1 ml of any gas at STP contain?
(1) 6.02×10^{23}; (2) 2.7×10^{23}; (3) 3.01×10^{20}; (4) 6.02×10^{20}; (5) 2.7×10^{19}.
2. The density of a gas with respect to helium is 19.5. What is the molecular weight of this gas?
(1) 19.5; (2) 39.0; (3) 58.5; (4) 78.0; (5) 97.5.
3. 0.05 g of a metal displaces 28 ml of hydrogen from an acid (the volume is given at STP; the water vapour pressure is taken into consideration). What is the equivalent weight of the metal?
(1) 5 g; (2) 1 g; (3) 15 g; (4) 20 g; (5) 25 g.
4. What quantity (in grams) of an oxide of 3 g of a metal with the equivalent weight of 12 g can be prepared?
(1) 3 g; (2) 6 g; (3) 5 g; (4) 10 g; (5) 12 g.
5. What is the equivalent weight of phosphoric acid in the following reaction?
$2H_3PO_4 + Ca(OH)_2 = Ca(H_2PO_4)_2 + 2H_2O$
(1) 1/3 mole; (2) 1/2 mole; (3) 1 mole; (4) 1/6 mole; (5) 2 moles.

EXPERIMENT 3. DERIVING FORMULAS OF CRYSTAL HYDRATES

Apparatus and reagents	Desiccator. Crucible tongs or surgical forceps. Crucible No. 2. Clay triangle. Mortar and a pestle. Sand bath. Blue vitriol.
Chemical balance with a set of weights.	

Crystal hydrates are substances which are crystallized with one or more water molecules. When heated to a certain temperature, some crystal hydrates only lose their water of crystallization, while decompose at higher temperatures. For example, copper sulphate crystal hydrate loses its water at a temperature of 258°C to convert into the anhydrous salt, which is then decomposed at 653°C.

Procedure. Calcine a porcelain crucible, then cool it in a desiccator and weigh on a chemical balance to an accuracy of 0.02 g. Place

about 1-1.3 g of powdered copper (or magnesium) sulphate crystal hydrate into the crucible and weigh on the same balance. Calculate the mass of the salt. Place the crucible onto a sand bath and heat at 240-260°C for 30-40 minutes. (Observe the colour change of copper sulphate.) As soon as the salt is white, remove the crucible from the sand bath using tongs, transfer it into the desiccator and allow it to cool there (10-20 minutes).

Why cannot the crucible with the salt be cooled in air?

Remove the cold crucible from the desiccator and weigh again.

Place the crucible on the sand bath again and heat for another 10-15 minutes. Cool the crucible in the desiccator and weigh again. Repeat this procedure till the difference in two subsequent weighings does not exceed 0.02 g.

Recording the results. Write down your results and observations into the log-book:

Mass of crucible, m_1, g.

Mass of crucible with crystal hydrate, m_2, g.

Mass of crystal hydrate, $m_3 = m_2 - m_1$, g.

Mass of crucible with salt after the 1st, 2nd, 3rd, and other calcinings: m_4', g; m_4'', g; m_4''', g.

Constant mass of crucible with anhydrous salt, m_4, g.

Mass of water lost, $m_5 = m_2 - m_4$, g.

Mass of anhydrous salt, $m_6 = m_4 - m_1$, g.

Calculate the number of moles of water per mole of anhydrous salt and derive the chemical formula of the crystal hydrate.

Note: If an analytical balance is used, the weight of sample can be decreased to 0.05-0.03 g.

EXPERIMENT 4. DETERMINING MOLECULAR WEIGHT OF CARBON DIOXIDE

Apparatus and reagents

Chemical balance with a set of weights.
Graduated cylinder, 1000-ml.
Compressed carbon dioxide cylinder or a Kipp gas generator with two absorbers.
Volumetric flask, 500-1000-ml, with a stopper. Thermometer. Pressure gauge. Glass writing pencil (wax).
Marble,
Hydrochloric acid (density 1.19 g/cm^3).
Sulphuric acid (density 1.84 g/cm^3).

Procedure. Close a dry flask with a stopper tightly and mark the level to which the stopper has passed into the neck (using the glass writing pencil). Weigh the flask with the stopper on a chemical balance to an accuracy of 0.02 g (m_1).

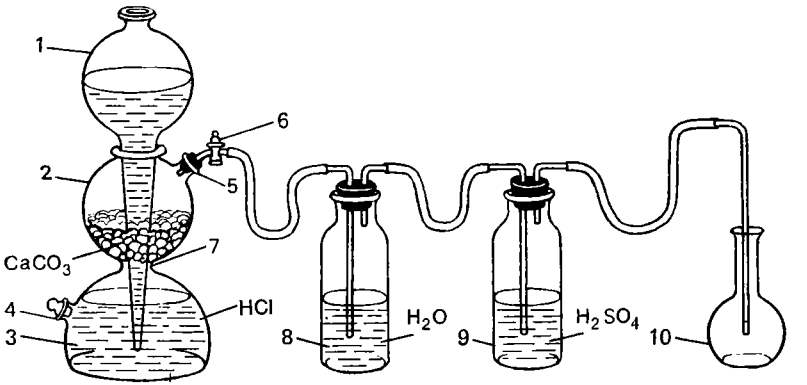


Fig. 26.
Apparatus for preparing and purifying carbon dioxide including the Kipp generator, wash bottles and CO_2 receptacle:
1–upper bulb; *2*–central bulb; *3*–acid reservoir; *4* and *5*–tubules; *6*–tap; *7*–throat; *8* and *9*–absorbers; *10*–CO_2 receptacle

Fill flask *10* (Fig. 26) with carbon dioxide, either from a compressed gas cylinder or a Kipp gas generator. The generator consists of two parts. The lower part includes central bulb *2* and acid reservoir *3*, which are interconnected through throat *7*. The upper bulb *1* is actually a funnel whose stem reaches to the bottom of acid reservoir *3*. The upper part of central bulb *2* has tubule *5*, which is closed with a stopper provided with a gas-discharge tube containing tap *6*. Acid reservoir also has tubule *4* to drain off the liquid. The generator is charged with solid substance through tubule *5*. The lumps of material should be large enough as not to fall into the acid reservoir. A round gasket is placed into throat *7* to separate the stem of the funnel from the throat walls. It has perforations through which liquid can pass. After the central bulb is loaded, tubule *5* is closed with a stopper with the tube. Tap *6* is opened and acid is poured into the funnel in amount sufficient to cover the solid in the central bulb. (Excess acid is undesirable.) The reaction between the solid and the acid thus begins and gas is liberated.

Tap *6* is closed and if the apparatus is tight, the acid is displaced from central bulb *2* into the acid reservoir and the upper bulb by the gas which is liberated during the reaction. As soon as the acid is displaced from the central bulb, the reaction stops and gas is no longer liberated.

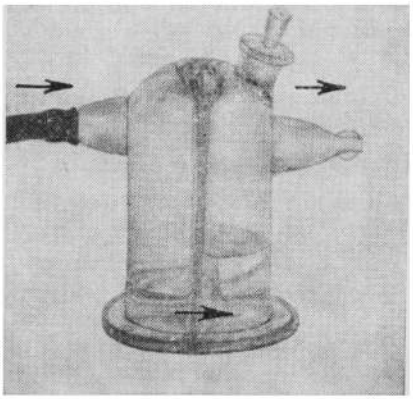


Fig. 27.
Tishchenko bottle

In order to resume liberation of gas, tap *6* is opened and the acid rises into the central bulb again to react with the solid contained in it. In order to discontinue the reaction, tap *6* is closed.

Carbon dioxide is prepared by the reaction between marble (whose small lumps are placed in central bulb *2*) and hydrochloric acid which is poured through the upper bulb *1*. Why cannot sulphuric acid be used for the purpose?

The obtained carbon dioxide should be purified from admixtures of hydrogen chloride and dried from water. To that end the liberated gas is passed through two absorbers (Fig. 26). Bottle *8* is filled with water to trap hydrogen chloride, while bottle *9* contains sulphuric acid which absorbs water from the gas. Tishchenko bottles (Fig. 27) can be used for the purpose.

Gas should be delivered into the receptacle in a slow stream so that bubbles could be counted in the absorbers. In 15-20 minutes, remove carefully the gas-discharge tube from the receptacle (flask *10*) and close the flask immediately with a stopper. In order to prevent heating carbon dioxide in the flask by the heat of the hands, hold the flask with your fingers by the neck in the vertical position when closing it with the stopper. Explain the cause of this precaution.

Weigh the flask containing carbon dioxide on the same balance and to the same accuracy as the flask filled with air was weighed (m_2).

Carry out a control test: collect the gas into the same flask for another 5 minutes and weigh the flask. If all air is displaced from the flask by carbon dioxide, the results of the first and second weighing should not differ by more than 0.02 g.

Measure the volume of the flask to the mark (V_1). To that end fill the flask with distilled water to the mark and measure this volume of water by transferring it into a graduated cylinder.

Note the atmospheric pressure and temperature during the experiment.

Results and calculations. Write down the results of the experiment in the following form:

Mass of flask with stopper and air, m_1, g.
Mass of flask with stopper and carbon dioxide, m_2, g.
Gas volume in flask, V_1, ml.
Temperature, t, °C; absolute temperature T, K.
Atmospheric pressure, p.

Calculate the volume of gas V_0 at STP using the Clapeyron equation:

$$\frac{V_0 p_0}{T_0} = \frac{V p}{T}$$

Calculate the mass of air m_3 and of hydrogen m_4 in the flask volume, remembering that at 0°C and 760 mm Hg one litre of air weighs 1.293 g and that of hydrogen, 0.089 g.

Calculate the mass of an empty (without air) flask with the stopper, $m_5 = m_1 - m_3$.

Determine the relative density of carbon dioxide with respect to air ρ_{air} and hydrogen ρ_H. Calculate the molecular mass of CO_2 using the following equations:

(a) $M = 29\rho_{air}$ (c) $M = \frac{m_6}{V_0} 22.4$

(b) $M = 2\rho_H$ (d) $M = \frac{m_6 T}{pv}$

Determine the absolute and relative errors of the experiment.

EXPERIMENT 5. DETERMINING THE EQUIVALENT MASS OF A METAL

Apparatus and reagents

Apparatus for determining equivalent mass of a metal. Analytical balance and weights. Thermometer. Pressure gauge. 25-50 ml graduated cylinder. Beaker, 50-ml. Funnel with a long stem. Filter paper. Sample of a chemically pure metal, about 0.1 g. Hydrochloric acid, 2 N solution.

Procedure. The experiment is performed in an apparatus shown in Fig. 28. It consists of 100-ml burette *1*, levelling bottle *2*, and glass tee *3*. A rubber tube with a clamp is attached to one end of the tee, the other end is provided with rubber stopper *4* which is used to close the burette. The third end of the tee is attached to Ostwald bottle *5*.

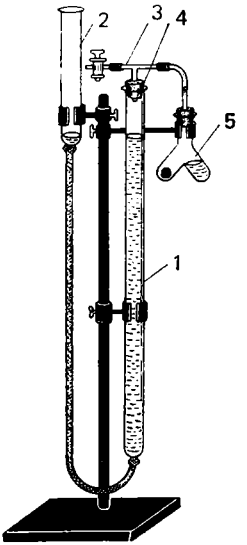


Fig. 28.
Apparatus for determining equivalent mass of metal:
1–burette, 100-ml;
2–levelling bottle;
3–T-piece; *4*–rubber stopper;
5–Ostwald flask

Weigh about 0.1 g of a metal to an accuracy of 0.0002 g on an analytical balance (on a weighed watch glass), transfer it into one arm of the Ostwald flask, and pour 10-12 ml of a 2 *N* hydrochloric acid into the other arm. Fasten the Ostwald flask in the stand and attach to the tee. Close the Ostwald flask and the burette tightly with stoppers. Open the clamp on the tee and using levelling bottle *2*, adjust the water level in burette *1* at the "0" mark (the bottom of the water meniscus should coincide with zero). Close the clamp and test the apparatus for tightness. To that end lower the levelling bottle so that the water level in it is below the water level in the burette. Fasten the levelling bottle in this position. As the levelling bottle is lowered, the water level in the burette lowers slightly as well. If the water level remains constant for another 1-2 minutes, the apparatus can be considered tight. Is the mass of the gas in the sealed apparatus changed when the levelling bottle position is changed? How does the gas pressure inside the bottle change (as related to atmospheric pressure) if the water level in the burette is (a) above that in the levelling bottle; (b) below the water level in the bottle, and (c) at the same level?

Having tested the apparatus for tightness, incline the stand without raising the levelling bottle, and transfer the acid into the other arm where the metal is. Liberation of hydrogen begins immediately and water is displaced from the burette into the levelling bottle. When the reaction is over, wait for 10-15 minutes so that the temperature of the gas inside the apparatus equals the ambient temperature.

Align the water levels in the burette and the levelling bottle and, if the water level remains constant for 1 minute, determine the volume of hydrogen liberated by reading the graduations from zero to the water level.

Results and calculations. Describe your observations in the laboratory log-book. Answer the questions. Record the results, following this form:

Mass of glass, m_1, g.
Mass of glass with metal sample, m_2, g.
Mass of metal, $m_3 = m_2 - m_1$, g.
Volume of hydrogen liberated during the reaction, V, ml.
Temperature, t, °C.
Absolute temperature, T, K.
Atmospheric pressure, p.
Saturated water vapour pressure at a given temperature, p_{H_2O} (see Appendix, Table 2).
Partial pressure of hydrogen, $p_{H_2} = p - p_{H_2O}$. Calculate the equivalent mass of the metal by two methods.

1. Calculate the mass of liberated hydrogen using the Clapeyron-Mendeleev equation $p_{H_2}V = (m/M)\,RT$. Calculate the equivalent mass of the metal using the law of equivalent masses.
2. Reduce the volume of liberated hydrogen to normal conditions using the Clapeyron equation: $V_0p_0/T_0 = Vp/T$. Once the volume of the equivalent mass of hydrogen is known, calculate the equivalent mass of the metal.

Draw a sketch of the apparatus that was used in the experiment.

EXPERIMENT 6. DETERMINING THE EQUIVALENT MASS OF SODIUM CARBONATE*

Apparatus and reagents

Flask, 50-ml, with a gas-discharge tube (assembled of glass and rubber tubes). Graduated cylinder, 100-ml. Crystallizer. Glass slide. Sodium carbonate, anhydrous. Sodium chloride, saturated solution. Hydrochloric acid, 2 *N* solution.

Procedure. Determine the equivalent mass of sodium carbonate from the known equivalent mass of carbon dioxide. Half fill crystallizer *1* (Fig. 29) with a saturated sodium chloride solution in which the solubility of carbon dioxide is lower than in water. Fill measuring cylinder *2* with the same solution to the top and cover with a glass slide (moving it smoothly). Turn the cylinder upside down and

* Equivalent mass of any other metal carbonate can be determined by this method.

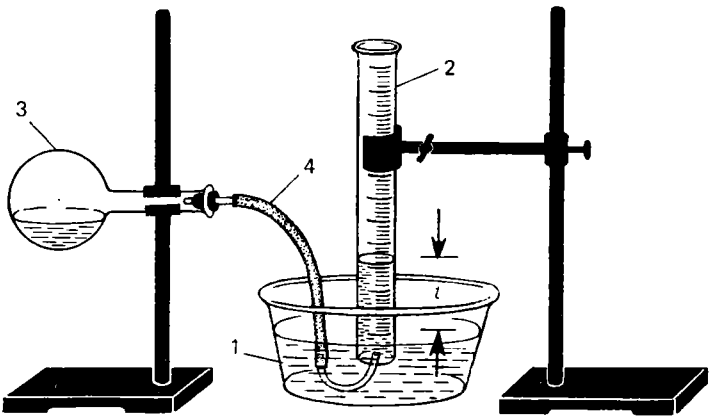


Fig. 29.
Apparatus for determining equivalent mass of sodium carbonate:
1–crystallizer;
2–measuring cylinder;
3–flask; *4*–gas tube
(glass and rubber tubes)

lower into a crystallizer. Remove the glass slide under solution and fix the cylinder in the stand so that the cylinder edges are below the solution level in the crystallizer, and seeing to it that no air enters the cylinder.

Place 8-10 ml of a 2 *N* hydrochloric acid solution into a 50-ml flask, wipe its neck with filter paper, and fix in the stand in the horizontal position. Using an analytical balance, weigh a watch glass with a piece of tissue paper (4 × 4 cm) to an accuracy of 0.001 g. Place 0.3-0.4 g of sodium carbonate on the paper and weigh again to the same accuracy. Place the salt together with the paper into the flask neck so that the salt crystals do not drop into the acid. Close the flask with a stopper containing a gas-discharge tube. Put the end of the tube into the mouth of the overturned cylinder. Dismantle the flask from the stand and transfer slowly (to prevent vigorous liberation of carbon dioxide) sodium carbonate into the acid (in small portions) by carefully tilting the flask. At the end of the experiment, push the paper with remaining crystals into the flask. When the evolution of the gas stops, fix the flask in the stand again. Measure the volume of the liberated carbon dioxide in the cylinder by measuring the distance *l* from the water level in the cylinder. Write down the ambient temperature and atmospheric pressure.

Recording the results and calculations. Draw a sketch of the apparatus. Record the results of the experiment:

Mass of watch glass with paper, m_1, g.
Mass of watch glass with paper and salt, m_2, g.
Mass of sodium carbonate, $m_3 = m_2 - m_1$, g.
Volume of liberated carbon dioxide, V, ml.
Distance from water level in crystallizer to water level in cylinder, l, mm.
Temperature, t, °C.
Atmospheric pressure, p.

Using the Clapeyron-Mendeleev equation

$$p_{CO_2}V = \frac{m}{M}RT$$

calculate the mass m of carbon dioxide. In order to determine pressure p_{CO_2}, subtract the pressure of the column of the solution p_s from atmospheric pressure p. The p_s should be calculated by the formula

$$p_s = \frac{\rho_s'}{\rho_{Hg}} l$$

The density of the saturated sodium chloride solution $\rho_s = 1.20$ g/cm³, and of mercury $\rho_{Hg} = 13.60$ g/cm³. Since the partial pressure of water vapour in saturated table salt solution is small, it can be disregarded. Thus

$$p_{CO_2} = p - p_s$$

Since the equivalent mass of the acid oxide CO_2 involved in the neutralization reaction with formation of Na_2CO_3 is half the mass of its mole, one can use the law of equivalents

$$Eq_{Na_2CO_3} / Eq_{CO_2} = m_3/m_{CO_2}$$

and calculate the equivalent mass of Na_2CO_3. Find the absolute and relative error of determination.

4 Rate of Chemical Reactions. Chemical Equilibrium

QUESTIONS AND PROBLEMS

1. Write down the expression for the rate of the following reactions:

(a) $2A + B = A_2B$ (c) $CO_2 + C = 2CO$
(b) $N_2 + O_2 = 2NO$ (d) $FeO + H_2 = Fe + H_2O$

How does the rate of reactions (a) and (b) change when the concentration of the reactants is doubled?

2. A flask with a capacity of 0.5 l contains 0.03 mole of nitrogen dioxide at a given temperature and pressure. Calculate the constant k_1 for the forward reaction occurring according to the equation $2NO_2 = N_2O_4$, if the reaction rate under these conditions is 1.08 mol/(l × s).
Answer: $k_1 = 300$ l/(mol × s).
3. The constant for the reaction $A + 2B = AB_2$ is 2×10^{-3} l/(mol × s). Determine (a) the rate v_1 of this reaction at the initial moment if the concentration of A is equal to that of B (0.4 mol/l), (b) the rate v_2 of this reaction in a certain time t, if 0.1 mol/l of substance AB_2 is formed by this moment.
Answer: (a) $v_1 = 1.28 \times 10^{-4}$ mol/(l × s); (b) $v_2 = 2.4 \times 10^{-5}$ mol/(l × s).
4. How do the rates of forward and reverse reactions

(a) $H_2 + Cl_2 \rightleftarrows 2HCl$ (c) $N_2O_4 \rightleftarrows 2NO_2$
(b) $2H_2 + O_2 \rightleftarrows 2H_2O$ (d) $CO_2 + C \rightleftarrows 2CO$

change if, at constant temperature, the concentration of each reactant is halved or tripled?
Write down the rate for each reaction and make the corresponding calculations.
5. How do the rates of forward and reverse reactions change if the volume of the system is doubled at constant temperature?

(a) $N_2 + O_2 \rightleftarrows 2NO$
(b) $2C + O_2 \rightleftarrows 2CO$
(c) $CO_2 + C \rightleftarrows 2CO$

Carry out the corresponding calculations and indicate the direction in which the chemical equilibrium will be shifted in each case.
6. Calculate the temperature coefficient for the rate of reaction if, when the temperature rises: (a) from 10 to 50°C, the reaction rate increases by 16 times; and (b) from 50 to 100°C, the rate increases by 1200 times.
Answer: (a) 2; (b) 4.13.
7. The temperature coefficient for the rate of a reaction is 1.5. How will the rate of this reaction change if the temperature rises by 30°C?
Answer: increases 3.4 times.
8. As the temperature of a reaction increases by 10°C, its rate is doubled. How will the rate of this reaction change if the temperature is raised by 50 and 20°C?
Answer: (1) increases 32 times, (2) increases 4 times.
9. How much should the temperature of the reaction be increased in order to accelerate its rate by 81 times if the temperature coefficient for the reaction rate is 3?
Answer: by 40°C.
10. Write down equilibrium constants for the following reactions:

(a) $2NH_3 \rightleftarrows 3H_2 + N_2$
(b) $Fe_3O_4 + 4CO \rightleftarrows 3Fe + 4CO_2$
(c) $3Fe_2O_3 + H_2 \rightleftarrows H_2O$ (vapour) $+ 2F_3O_4$
(d) $C + CO_2 \rightleftarrows 2CO$

In what direction will the chemical equilibrium shift in each of these reactions if pressure is increased?
11. In what direction will the chemical equilibrium of the following reversible reactions

(a) $2SO_2 + O_2 \rightleftarrows 2SO_3 + 192.74$ kJ (46 kcal)
(b) $N_2O_4 \rightleftarrows 2NO_2 - 54.47$ kJ (13 kcal)

shift if temperature is decreased or pressure is decreased?
12. How can the chemical equilibrium in the following reactions be shifted to the right?

(a) $C + H_2O$ (vapour) $\rightleftarrows CO + H_2 - 129.89$ kJ (31 kcal)
(b) $N_2 + 3H_2 \rightleftarrows 2NH_3 + 92.18$ kJ (22 kcal)

13. Calculate the equilibrium constant K for the reaction $2HBr \rightleftarrows H_2 + Br_2$ if the initial mass of hydrogen bromide is 0.809 g and 5% of it has reacted by the moment when the chemical equilibrium was attained?
Answer: $K = 0.9 \times 10^{-4}$.
14. 0.5 mole of hydrogen and 0.5 mole of nitrogen were placed in a 500-ml flask. By the time equilibrium has been reached, 0.02 mole of ammonia has formed at a certain temperature. Calculate the equilibrium constant for a given system.
Answer: $K = 1.97 \times 10^{-3}$.
15. The following reaction occurs in a 500-ml flask $CH_4 + H_2O$ (vapour) $\rightleftarrows$ $\rightleftarrows CO + 3H_2$. Calculate the equilibrium constant for this system if the initial masses of the reactants in a given volume are: CH_4 — 0.8 g, H_2O — 0.9 g, CO — 1.4 g, H_2 — 0.1 g; by the time chemical equilibrium has been attained, 50% of methane has already reacted.
Answer: $K = 9.37 \times 10^{-1}$.
16. At a certain temperature, the composition of a system at equilibrium in a volume of 10 litres is the following: CO — 11.2 g, Cl_2 — 14.2 g, and $COCl_2$ — 19.8 g. Calculate the equilibrium constant K of the reaction $CO + Cl_2 \rightleftarrows COCl_2$ under a given conditions.
Answer: $K = 25$.
17. Calculate the equilibrium constant for the reaction $N_2 + 3H_2 \rightleftarrows 2NH_3$, if 1.4 g of nitrogen and 1 g of hydrogen are placed into a vessel with a capacity of 10 litres. It is known that 0.85 g of ammonia has been formed in the system by the time chemical equilibrium has been attained.
Answer: $K = 6.9$.
18. The equilibrium constant K of the reaction $2NO_2 \rightleftarrows N_2O_4$ at a certain temperature is 0.3. Calculate the concentration of the components at the moment of equilibrium, if the initial concentration of NO_2 is 9.2 g/l.
Answer: $[NO_2] = 0.18$ mol/l; $[N_2O_4] = 0.01$ mol/l.
19. Determine the initial concentration of nitrogen and hydrogen (in mol/l and in g/l) if the concentrations of these substances in the system $N_2 + 3H_2 \rightleftarrows$ $\rightleftarrows 2NH_3$ at equilibrium are (in mol/l): N_2 — 0.5, H_2 — 0.3, and NH_3 — 2.
Answer: N_2 — 1.5 mol/l or 42 g/l; H_2 — 3.3 mol/l or 6.6 g/l.
20. At a certain temperature, 21.2 moles of hydrogen and 5.23 moles of iodine were mixed in a closed vessel. Determine the composition of this mixture at equilibrium (in mol/l), if the equilibrium constant of the reaction $H_2 + I_2 \rightleftarrows$ $\rightleftarrows 2HI$ is 50.
Answer: $H_2 = 16$ mol/l, $I_2 = 0.13$ mol/l, $HI = 10.2$ mol/l.
21. The equilibrium constant of the reaction $CH_3COOH + C_2H_5OH \rightleftarrows$ $\rightleftarrows CH_3COOC_2H_5 + H_2O$ is 4. Calculate concentrations of all components in this system at equilibrium if their initial concentrations were as follows: acetic acid—2 mol/l and alcohol—1 mol/l.
Answer: $[CH_3COOH] = 1.155$ mol/l; $[C_2H_5OH] = 0.155$ mol/l; $[CH_3COOC_2H_5] =$ $= [H_2O] = 0.845$ mol/l.
22. Determine the percent composition (by volume) of gases in a mixture $C + O_2 \rightleftarrows CO_2$ at equilibrium, if the equilibrium constant of this reaction at a certain temperature is 0.289.
Answer: CO_2 — 22.6%; O_2 — 77.4%.
23. Equilibrium is attained at a certain temperature in the system $CO + H_2O$ (vapour) $\rightleftarrows CO_2 + H_2$. The quantities of the components, in moles, are the following: CO — 0.8, H_2O (vapour) — 7.2, CO_2 — 2.4, and H_2 — 2.4. Determine the mass of each component in the system if 2 moles of CO are added into the reaction volume at the same temperature.
Answer: 148.3 g of CO_2; 6.7 g of H_2; 112.1 g of H_2O; 51.2 g of CO.
24. Determine the equilibrium constant of the reaction $CO_2 + H_2 \rightleftarrows CO +$ $+ H_2O$ (vapour), if at a temperature of about 500°C the mixture at equilibrium

contains 4% of CO_2, 64% of H_2, 16% of H_2O and 16% of CO. Calculate the initial concentrations of carbon dioxide and hydrogen (in per cent).
Answer: $K = 1$; $[CO_2] = 20\%$; $[H_2] = 80\%$.
25. At equilibrium, the system $CO_2 + H_2 \rightleftarrows CO + H_2O$ (vapour) contains (in mole/litre): 0.004 of CO_2, 0.001 of H_2, 0.02 of CO, and 0.02 of H_2O. Calculate the equilibrium constant and the initial concentrations of carbon dioxide and hydrogen. The initial concentrations of carbon monoxide and water were 0.
Answer: $K = 1 \times 10^{-2}$; $[CO_2] = 0.024$ mol/l; $[H_2] = 0.021$ mol/l.
26. At a certain temperature and pressure the system at equilibrium $4HCl + O_2 \rightleftarrows 2Cl_2 + 2H_2O$ occupies a volume of 0.5 litre and contains 3.65 g of HCl, 3.2 g of O_2, 7.1 g of Cl_2 and 1.8 g of H_2O. Calculate the equilibrium constant of this reaction and the initial concentration of the reactants in mol/l and g/l, if the initial concentrations of chlorine and water are zero.
Answer: $K = 5$; $[HCl] = 0.6$ mol/l or 21.9 g/l; $[O_2] = 0.3$ mol/l or 9.6 g/l

Examples of Multiple-choice Questions

1. How will the reaction rate increase if the temperature of the reaction is increased from 40 to 70°C? The temperature coefficient is 3.
(1) 3 times; (2) 18 times; (3) 30 times; (4) 27 times; (5) 9 times higher.
2. How will the rate of the forward and reverse reaction $2O_2 \rightleftarrows 2O + O_2$ increase in a closed system if the pressure is increased 3 times?
(1) forward — 6 times, reverse — 9 times; (2) forward — 9 times, reverse — 27 times; (3) forward — 36 times, reverse — 94 times; (4) forward — 3 times, reverse — 6 times; (5) forward — 18 times, reverse — 54 times.
3. Equilibrium concentrations of hydrogen iodide, iodine, and hydrogen are 0.3 mol/l each. What is the initial concentration of hydrogen iodide in the system $2HI \rightleftarrows H_2 + I_2$, if the initial concentrations of iodine and hydrogen are 0?
(1) 0.6; (2) 1.2; (3) 2; (4) 0.9; (5) 1.8.
4. Which of the following expressions corresponds to the equilibrium constant of the reaction $3Fe + 4H_2O$ (vapour) $\rightleftarrows Fe_3O_4 + 4H_2$ (g)?

(1) $K = \dfrac{[H_2]^4}{[H_2O]^4}$ (2) $K = \dfrac{[H_2]}{[H_2O]}$

(3) $K = \dfrac{[Fe_3O_4][H_2]}{[Fe]^3[H_2O]^4}$ (4) $K = \dfrac{[Fe_3O_4][H_2]}{[Fe]^3[H_2O]^4}$

(5) $K = \dfrac{[H_2]^4}{[H_2O]}$

5. How will the lowering of the temperature affect the chemical equilibrium in the system

$2NO + O_2 = 2NO_2$, $\Delta H < 0$

(1) the equilibrium will not be upset; (2) the equilibrium will be shifted to the left; (3) the equilibrium will be shifted to the right.

EXPERIMENT 7. RATE OF CHEMICAL REACTION AND CHEMICAL EQUILIBRIUM

Apparatus and reagents

Stopwatch.
Thermostat (three 200-250-ml beakers) provided with a lid with holes for test tubes. Graduated cylinder, 10-ml.
Thermometer, scale reading to 50 °C.

Glass rods. Dropping pipettes. Filter paper. Spatula. Mortar with a pestle. Sodium sulphite, crystalline.

Manganese dioxide.

Calcium carbonate (chalk). Mercury(II) nitrate. Potassium iodide. Potassium chloride. Lead nitrate. Solutions: sodium iodate, 0.02 *N*; sodium thiosulphate, 1 *N* and 0.5 *N*; sulphuric acid, 2 *N*; hydrochloric acid (density 1.19 g/cm^3); starch solution; ferric chloride, 0.0025 *N*, 0.5 *N* and saturated; potassium thiocyanate, 0.0025 *N* and saturated; potassium permanganate, 0.5 *N*; copper sulphate, 0.5 *N*; potassium dichromate, 0.1 *N*; hydrogen peroxide, 3%.

The apparatus needed for part 5 of this experiment is shown in Fig. 28. Apparatus for shifting chemical equilibrium in a gaseous system (part 6, *B*) is shown in Fig. 30.

1. Effect of Reactant Concentration on the Reaction Rate in a Homogeneous System

A. Reaction between sodium iodate and sodium sulphite

Oxidation of sodium sulphite with sodium iodate is expressed by the overall equation:

$$2NaIO_3 + 5Na_2SO_3 + H_2SO_4 = I_2 + 6Na_2SO_4 + H_2O$$

This reaction proceeds in steps:

$$NaIO_3 + 3Na_2SO_3 = NaI + 3Na_2SO_4 \qquad (I)$$

$$IO_3^- + 3SO_3^{2-} = I^- + 3SO_4^{2-}$$

After all sodium sulphite has been oxidized (the first stage), the formed sodium iodide reacts with unreacted sodium iodate:

$$NaIO_3 + 5NaI + 3H_2SO_4 = 3I_2 + 3Na_2SO_4 + 3H_2O \qquad (II)$$

$$IO_3^- + 5I^- + 6H^+ = 3I_2 + 3SO_4^{2-} + 3H_2O$$

Molecular iodine reacts with starch present in the solution to give a blue compound that colours the solution. The blue colour indicates the beginning of the second stage and termination of the first one. Can free iodine be formed in the presence of Na_2SO_3? Since oxidation of the sulphite with iodate is a slow reaction, its duration can be measured by a stopwatch. Start counting seconds from the moment when sodium sulphite is added to the iodate solution and assume the appearance of blue colour as the end of the reaction.

Procedure. Prepare equal volumes of sodium iodate solutions of different concentration in two dry test tubes. To that end, place 4 drops of a 0.02 *N* sodium iodate solution into one test tube and add 12 drops of distilled water. Place 8 drops of the same solution of sodium iodate into the other test tube and add 8 drops of distilled water. The sodium iodate concentration in the second test tube is twice as higher as in the first one. If the concentration of sodium iodate in the first test tube is assumed to be *c* moles, the concentration in the

second test tube is $2c$ moles. Put the test tubes in the rack and stir the solutions using glass rods (leave the glass rods in the test tubes).

Prepare a reducing solution. To do so, place two microspatulas of sodium sulphite into a test tube and dissolve in ten drops of water. Add 10 drops of freshly prepared starch solution and two drops of a 2 *N* sulphuric acid solution. Stir the solution using a glass rod. Start the stopwatch. Add two drops of freshly prepared reducing solution into test tube No. 1. Determine the time from the moment of the addition of the reducing mixture to the moment when the solution turns blue.

Add two drops of the same reducing mixture to test tube No. 2, and measure the time again. How does the reaction rate change with changing concentration of sodium iodate in test tubes Nos. 1 and 2?

Recording the results. Write down the results of the experiment in the following table:

Test tube No.	Q-ty of drops of $NaIO_3$	Q-ty of drops of H_2O	Q-ty of drops of reducing solution	Total volume of solution (q-ty of drops)	Concentration of $NaIO_3$	Reaction time, as determined by stopwatch	Reaction rate, $1/t$ in conv. units (t, s)
1	4	12	2	18	c		
2	8	8	2	18	$2c$		

B. Reaction of sodium thiosulphate with sulphuric acid

The reaction of sodium thiosulphate with sulphuric acid occurs by the following equation:

$$Na_2S_2O_3 + H_2SO_4 = Na_2SO_4 + S + SO_2 + H_2O$$

Procedure. First carry out a qualitative test: place 5-10 drops of a 1 *N* sodium thiosulphate solution into a test tube and add 3-5 drops of a 2 *N* sulphuric acid solution. Observe slight opalescence and further turbidity of the solution due to precipitation of free sulphur.

Prepare three solutions of sodium thiosulphate of various concentrations. To do so, place 5 drops of a 1 *N* sodium thiosulphate solution and 10 drops of water into the first test tube, 10 drops of the same 1 *N* sodium thiosulphate solution and 5 drops of water into the second test tube, and 15 drops of the same solution into the third test tube. Shake carefully the first and second test tubes. The concentration of $Na_2S_2O_3$ (in moles) in the first test tube is thus c, in the second test tube $2c$, and in the third $3c$.

Start the stopwatch. Add a drop of a 2 *N* sulphuric acid solution to test tube No. 1 and measure the time that passes till vivid opalescence appears. Add a drop of a 2 *N* sulphuric acid solution to test tubes Nos. 2 and 3 and determine the time when opalescence develops.

Recording the results. Write down the test results into the table. Plot the graph to illustrate the dependence of the reaction rate on concentration of the reactants. Indicate relative concentrations of sodium thiosulphate solution along the abscissas and the corresponding reaction rates along the ordinates.

2. Effect of Temperature on Reaction Rate in a Homogeneous System

Two thermostats are required for the experiment. The temperature in one of them is maintained 10°C and in the other 20°C above the ambient temperature. (Water baths covered with lids provided with three holes for a thermometer and two test tubes, as shown in Fig. 19, can be used.)

Procedure. Prepare three thermostats, Nos. 1, 2, and 3. To that end, fill three 200-250-ml beakers with water to 2/3 of their capacity. Keep one beaker on the bench at room temperature. Measure the temperature of water with thermometers. Place beakers Nos. 2 and 3 on asbestos-centred gauzes on a ring over burners. Heat water in beakers No. 2 and No. 3 to temperatures 10°C and 20°C above the temperature in beaker No. 1, respectively. Adjust the flame of the burners so that the water temperature remains constant (± 0.5°C). Cover each beaker with a lid provided with three holes. Place a thermometer with a scale reading to 50°C in one hole, the test tube containing a 2 *N* sulphuric acid solution (with a pipette inside it) in another, and the test tube with 10 drops of a 1 *N* sodium thiosulphate solution in the third hole.

Start a stopwatch in 10-15 minutes. Add a drop of a 2 *N* sulphuric acid from the test tube in thermostat No. 1 into the test tube containing sodium thiosulphate solution in the same thermostat. Determine the time that elapses from the moment when the acid was added to the moment when opalescence becomes noticeable.

Repeat the experiment with sodium thiosulphate and sulphuric acid solutions in thermostats Nos. 2 and 3. Determine the time of the reaction as described for thermostat No. 1.

Recording the results. Write down the obtained results into the following table:

No. of observation	Temperature of experiment, °C	Reaction time as measured by the stopwatch	Reaction rate, $1/t$

Make a conclusion on the dependence of the reaction rate on the temperature.

3. Effect of Surface Area of Reagents on Reaction Rate in Heterogeneous System

A. Reaction of mercury(II) nitrate with potassium iodide

Procedure. Place a few crystals of mercury(II) nitrate and potassium iodide into a dry test tube and about the same amount of the same substances but in the form of fine powder into another test tube. Shake vigorously both test tubes. Observe the colour change due to formation of mercury(II) iodide. Note the different reaction rates in the test tubes. How can this difference be explained? Write down the reaction equation.

B. Dissolution of calcium carbonate in hydrochloric acid

Procedure. Place a small piece of chalk on filter paper and crush to powder using a glass rod. Transfer the powder into a conical test tube. Place another lump of chalk of about the same size into another test tube, and add 10-20 drops (equal amounts) of hydrochloric acid (density 1.19 g/cm^3) to both test tubes. In order to ensure simultaneous addition of the acid, two students can perform the experiment. Note the time of complete dissolution of chalk in the test tubes.

Recording the results. Write down the reaction equation. Explain the different time of reactions in the two test tubes.

4. Effect of a Catalyst on Reaction Rate

A. Catalytic reduction of iron(III)

Procedure. Place 10 drops of a 0.5 *N* potassium thiocyanate solution, and a drop of a 0.5 *N* iron(III) chloride solution into each of two test tubes. Observe the reaction. Add a drop of a 1 *N* copper sulphate solution to one test tube, and 10 drops of sodium thiosulphate solution into both test tubes. Observe the different rate at which the solutions are decolourized as iron(III) is reduced with sodium thiosulphate to iron(II).

Recording the results. Describe your observations. Write down the equations for the following: (a) reaction between iron(III) chloride and potassium thiocyanate by which red $Fe(SCN)_3$ is formed; (b) reduction of iron(III) to iron(II) with sodium thiosulphate by the following equation

$$2Fe(SCN)_3 + 2Na_2S_2O_3 = Na_2S_4O_6 + 2Fe(SCN)_2 + 2NaSCN$$

What is the colour of $Fe(SCN)_2$? What substance is a catalyst in this reaction?

5. Determining Reaction Rate and Rate Constant of Hydrogen Peroxide Decomposition

In aqueous solution, hydrogen peroxide decomposes spontaneously by a slow reaction $2H_2O_2 = 2H_2O + O_2$. Some solid substances and also cations or anions of certain compounds act catalytically to accelerate this process. Depending on a particular substance used as a catalyst, this reaction in aqueous solutions can be heterogeneous or homogeneous. Potassium dichromate is a catalyst in this experiment and determines the homogeneous nature of this catalytic reaction.

Procedure. Apparatus shown in Fig. 28 is used in the experiment. Fill the levelling bottle and the burette with water. Drop from a pipette 5-6 drops of a 0.1 *N* potassium dichromate solution into one arm of the Ostwald flask and (using another pipette) 1 ml of a 3% hydrogen peroxide solution into the other arm. (Calculate the volume of oxygen that will be liberated during the reaction assuming the density of hydrogen peroxide to be 1 g/cm^3.) Connect carefully the Ostwald flask to the burette and close it tightly with a stopper. Open the clamp and using the levelling bottle adjust the water level in the burette at zero. Close the clamp and test the apparatus for tightness by raising and lowering the levelling bottle. If the apparatus is tight, adjust the liquid level in the burette at zero and fix the levelling bottle in the stand. Tilt the Ostwald flask carefully to transfer the hydrogen peroxide solution completely into the other arm. Start the stopwatch simultaneously. Observe the colour change which is due to formation of intermediate products of the catalytic reaction. Take the first measurement and note the liquid level in the burette and the time (as read off the stopwatch). During the first ten minutes, record the liquid level at 1-minute intervals and align the levels in the burette and the levelling bottle. During the next ten minutes, record the liquid level at 2-minute intervals. When the reaction is almost terminated due to a substantial decrease in the H_2O_2 concentration, arrest the stopwatch and lower the arm of the Ostwald flask, where the reaction took place, into hot water in a beaker for 4-6 minutes. Restoration of the initial colour of the solution (characteristic of potassium dichromate) indicates complete decomposition of the intermediate reaction products and complete decomposition of H_2O_2. Cool the apparatus for 5-10 minutes (to room temperature), reduce the pressure in the apparatus to the atmospheric one, and record the liquid level in the burette. Using the data of the experiment, construct a graph showing the dependence of the volume of the liberated oxygen on time and calculate the rate constant for four points of the curve in accordance with this equation:

$$k = \frac{\log V_t - \log (V_t - V_\tau)}{0.4343}$$

where V_t is the total volume of oxygen liberated and V_τ is the volume of oxygen liberated during time τ.

6. Shifting Equilibrium of Reversible Reactions

A. Effect of reactant concentration on chemical equilibrium

Procedure. Place 5-7 drops of a 0.0025 *N* ferric chloride and potassium thiocyanate solutions into each of four conical test tubes. Stir the solutions using glass rods and place the test tubes in the rack Keep one test tube as reference. Add the following reagents to the other test tubes: 1 drop of a saturated ferric chloride solution into the first test tube, 1 drop of a saturated potassium thiocyanate solution into the second, and several crystals of potassium chloride into the third test tube. Compare the colour intensity of the obtained solutions to that of the reference solution.

Recording the results. Describe your observations in the log-book. Write down the equation for the corresponding reversible reaction, the equilibrium constant and answer the following questions.

1. What substances are present in the studied solution at equilibrium?
2. Which particular substance accounts for the red colour of the solution?
3. How does the colour intensity change and in what direction is the equilibrium shifted in the system at equilibrium if we add (a) ferric chloride, (b) potassium thiocyanate, (c) potassium chloride?
4. How do the concentrations of the following components in the system at equilibrium change in each particular case: (a) ferric thiocyanate, (b) potassium chloride, (c) ferric chloride, (d) potassium thiocyanate as compared with their concentrations during the initial equilibrium?

B. Effect of temperature on chemical equilibrium

Procedure. Place lead nitrate in a cylindrical test tube to 1/4 its capacity and close with a stopper fitted with a bent tube. Fix the test tube in the stand and heat carefully over a small flame to complete decomposition of lead nitrate. Fill two dry microflasks with liberated nitrogen dioxide by lowering the end of the tube into the flasks. Communicate the microflasks through a bent tube (Fig. 30) with rubber tubings on its end used as stoppers for the microflasks. Note the brown colour of nitrogen dioxide. Place hot water into one beaker and ice and cold water into another. Lower simultaneously the two microflasks into the beakers and observe intensification of gas colour in the microflask in hot water and decolourization in cold water. A reversible reaction of dimerization of the brown nitrogen diox-

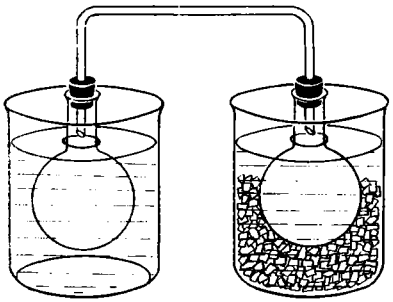


Fig. 30.
Apparatus for displacement of equilibrium in the system $2NO_2 \rightleftarrows N_2O_4$

xide NO_2 occurs with the formation of a colourless nitrogen dimer N_2O_4:

$2NO_2 \rightleftarrows N_2O_4$

Using the Le Chatelier principle and the experimental data determine the heat effect of the forward and reverse reactions.

5 Enthalpy of Chemical Reaction

QUESTIONS AND PROBLEMS*

1. Under what conditions is the heat effect of a chemical reaction numerically equal to the change in enthalpy?
2. The enthalpy of neutralization of various strong acids and bases is the same, while the enthalpy of neutralization of weak acids and bases depends on the nature of the reacting substances. Explain.
3. How does the heat of neutralization of strong acids with strong bases and the heat of water dissociation relate?
4. Calculate the enthalpy of conversion of 1 mole of oxygen into ozone from the oxidation reaction of As_2O_3 with oxygen and ozone:

$As_2O_3(c) + O_2(g) = As_2O_5(c) \quad \Delta H_1 = -270.8$ kJ/mol
$3As_2O_3(c) + 2O_3(g) = 3As_2O_5(c) \quad \Delta H_2 = -1096.3$ kJ/mol

Answer: +96.4 kJ/mol.
5. The enthalpies of dissolution in water of the crystal hydrate $CuSO_4 \cdot 5H_2O$ and of anhydrous copper sulphate are +11.7 and −66.1 kJ/mol, respectively. Calculate the enthalpy of the reaction by which 5 water molecules are added to a molecule of copper sulphate (calculate per 1 mole):

$CuSO_4(c) + 5H_2O(l) = CuSO_4 \cdot 5H_2O(c)$

Answer: +77.8 kJ/mol.
6. The enthalpies of dissolution in water of anhydrous soda and of the crystal hydrate $Na_2CO_3 \cdot 10H_2O$ are −25 and +67 kJ/mol, respectively. Calculate the enthalpy of addition of ten molecules of water to one sodium carbonate molecule.

* When solving Problems 7 and 8, consult Table 3 in Appendix.

Answer: +91.2 kJ/mol.

7. Calculate the enthalpy of the reaction

$2Cu_2O(c) + Cu_2S(c) = 6Cu(c) + SO_2(g)$

using enthalpies of formation of the substances involved in the reaction.
Answer: −115.5 kJ/mol.

8. Calculate standard enthalpy in the following reactions:

(a) $4NH_3(g) + 5O_2(g) = 4NO(g) + 6H_2O(g)$
(b) $4NH_3(g) + 3O_2(g) = 2N_2(g) + 6H_2O(g)$
(c) $Fe_2O_3(c) + 3CO(g) = 2Fe(c) + 3CO_2(g)$
(d) $CH_4(g) + 2O_2(g) = CO_2(g) + 2H_2O(g)$
(e) $2Mg(c) + CO_2(g) = 2MgO(c) + C(graphite)$
(f) $2Cl_2(g) + 2H_2O)(g) = 4HCl(g) + O_2(g)$
(g) $3CH_4(g) + CO_2(g) + 2H_2O(l) = 4CO(g) + 8H_2(g)$
(h) $CaO(c) + Fe_2O_3(c) = Ca(FeO_2)_2(c)$
(i) $2H_2S(g) + SO_2(g) = 3S(rhomb) + 2H_2O(l)$
(j) $2C_2H_2(g) + 5O_2(g) = 4CO_2(g) + 2H_2O(g)$
(k) $CaCO_3(c) = CaO(c) + CO_2(g)$

Examples of Multiple-choice Questions

1. Which of the following thermodynamic expressions describe exothermic reactions?

(1) $Q_p < 0$; (2) $\Delta S < 0$; (3) $\Delta S > 0$; (4) $\Delta H > 0$; (5) $\Delta H < 0$.

2. Indicate the equation for the reaction for which ΔH° is the enthalpy of formation of a substance:

(a) $CaO(c) + CO_2(g) = CaCO_3(c)$
(b) $C(c) + 2Cl_2(g) = CCl_4(g)$
(c) $CaO(c) + SiO_2(c) = CaSiO_3(c)$
(d) $Cu_2S(c) + O_2(g) = 2Cu(c) + SO_2(g)$
(e) $CF_4(g) = C(c) + 2F_2(g)$

3. Determine the enthalpy of conversion of graphite into diamond (in kJ/mol) using the following data:

C (graphite) + $O_2 = CO_2$ $\quad \Delta H^\circ = -390.32$ kJ/mol
C (diamond) + $O_2 = CO_2$ $\quad \Delta H^\circ = -392.24$ kJ/mol

1) +788.64; 2) +1.88; 3) −390.32; 4) −1.05; 5) −43.95.

4. During decomposition of 0.5 mole of CO_2, 196.7 kJ of heat is absorbed. Determine the enthalpy of formation of CO_2 (in kJ/mol).
1) +390; 2) −390; 3) −155; 4) +155; 5) +780.

5. The enthalpy of formation of which substance is equal to zero?
(1) H_2O_2; (2) H_2SO_4; (3) O_2; (4) $CaCO_3$; (5) O_3.

Explanatory Notes to Experiments 8, 9 and 10

Apparatus and reagents

Calorimeter.
Graduated cylinder, 200-ml. Chemical balance. Sodium carbonate, anhydrous.
Sodium carbonate, crystal hydrate. Sodium sulphate, anhydrous. Sodium sulphate, crystal hydrate.
Magnesium sulphate, anhydrous.
Magnesium sulphate, crystal hydrate.
Magnesium metal, ribbon. Solutions: sulphuric acid, 0.1 *N*; hydrochloric acid, 1 *N*; nitric acid, 1 *N*; sodium hydroxide, 1 *N*; potassium hydroxide, 1 *N*.

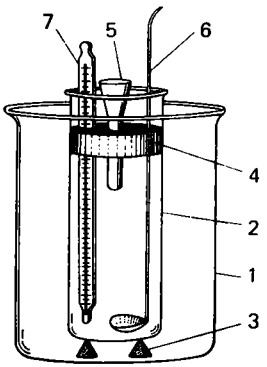


Fig. 31.
Calorimeter:

1–larger beaker;
2–reaction beaker;
3–support; *4*–cover;
5–funnel; *6*–stirrer;
7–thermometer

Enthalpy of chemical reactions can be determined in various calorimeters, the main requirement being adequate insulation of the vessel from the environment. A Dewar flask should be used in experiments in general chemistry. Or a simplified apparatus shown in Fig. 31 can be used. It consists of two beakers of different capacities placed in one another. The larger beaker *1* has a capacity of 500 ml, and the inner 250 ml. The smaller beaker is placed inside the larger one on a support *3* which may be cork or plexiglass. The inner beaker is covered with lid *4* made of plexiglass and provided with three holes for the stem of funnel *5*, stirrer *6*, and thermometer *7* with a scale graduated in 0.1°C. The stirrer can be operated by an electric motor or manually. The inner beaker can be made of stainless steel.

The amount of heat liberated or absorbed inside a calorimeter can be determined by the formula

$$q = (t_f - t_i) \sum C \qquad (1)$$

where t_f is the final temperature at the end of the reaction, t_i is the initial temperature, and $\sum C$ is the total heat capacity of the system which is made up of the heat capacities of the calorimetric vessel, calorimetric liquid and of the test substance. The total heat capacity of the system

$$\sum C = C_1 m_1 + C_2 m_2$$

where C_1 and m_1 are specific heat and mass of the reaction vessel; C_2 and m_2 are the same parameters for the liquid inside the calorimeter (the summary mass of water and the dissolved substance).

If a glass reaction beaker is used, the heat capacity of the calorimetric vessel can be disregarded because of its low heat conductivity. If the vessel is made of stainless steel, it should be weighed on a chemical balance (m_1) while the specific heat C_1 should be assumed to be 0.1 kcal/kg × °C or 0.42 kJ/(kg × K). Specific heat of solu-

tions and their densities should be assumed equal to those of water, i.e. specific heat should be 4.2 kJ/(kg × K), or 0.1 kcal/kg × °C and density 1 g/cm³. Equation (1) transforms then into
for a glass vessel

$$q = (t_t - t_1)\, m_2 \qquad (2)$$

for a stainless steel vessel

$$q = (t_t - t_1)\,(0.1m_1 + m_2)$$

The heat effect, as referred to 1 mole of a substance (Q_m), can then be determined from the formula

$$Q_m = q\,\frac{M}{m}$$

The enthalpy is then

$$\Delta H = -Q_m = -q\,\frac{M}{m} \qquad (3)$$

where M is the molar mass of the dissolved substance and m is the mass of the sample, g.

Procedure. All manipulations during determining enthalpies of chemical processes should be carried out in the same sequence. Using a graduated cylinder, measure out a definite volume of water or solution and pour it into the reaction beaker. Wait for 3-5 minutes until the temperature inside the calorimeter is the same as the ambient temperature. Then start measuring the temperature at 1-minute intervals (three measurements). If the temperature does not practically change, assume it to be t_1.

Now weigh out (or measure with a graduated cylinder) the amount of the test substance and place it into the liquid inside the reaction beaker (through a funnel). The mixture should be stirred continually. Measure the temperature of the solution at 30-second intervals until it changes gradually or remains constant (usually during 3-4 minutes). Take temperature at 1-minute intervals for another 3 minutes. Write down the results of your observation in the table:

Time from the start of experiment, min	0	0.5	1.0	1.5	2.0	2.5	3.0	3.5	4.0	4.5
Temperature, °C										

Construct a graph to show the change of temperature with time, plotting temperature along the axis of ordinates and time, in minutes, along the axis of abscissas. Figure 32 shows such a graph. Extrapolate the gradual linear temperature change of the final period to

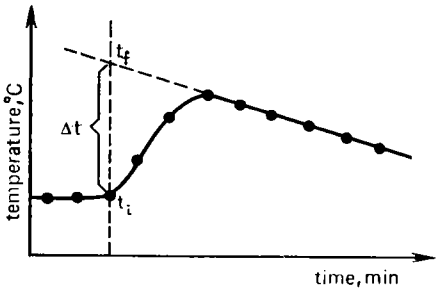


Fig. 32.
Variation of temperature depending on time

the initial moment of the reaction. This value is t_f—the final temperature of the process. The heat exchange of the calorimeter with the environment is taken into consideration. The value, which is necessary for calculations, is thus determined $\Delta t = t_f - t_1$.

EXPERIMENT 8. ENTHALPY OF SALT HYDRATION

The enthalpy of addition of crystallization water to an anhydrous salt can be determined from enthalpies of dissolution of an anhydrous salt and its crystal hydrate, using the Hess law. (Students can be given different salts.)

Procedure. Obtain an anhydrous salt and its crystal hydrate from the instructor. If a steel reaction beaker is used, weigh it on a chemical balance (m_1) and pour 25 ml of distilled water into it. (Do not weigh a glass reaction beaker.) Weigh (on a sheet of paper) 1.5-2 g of the anhydrous salt to an accuracy of 0.02 g and drop it into the calorimetric vessel. Continue the procedure as has been instructed above.

Repeat the experiment with the crystal hydrate of a given salt.

Recording the results and calculations.

Mass of anhydrous salt, m_s.

Mass of water, m_w.

Initial temperature, t_i.

Final temperature, t_f.

$\Delta t = t_f - t_1$

Calculate the enthalpy of dissolution of 1 mole of the anhydrous salt ΔH_1 using formula (3), assuming $C_1 = C_2 = 1$.

Make a similar record and calculate the enthalpy of dissolution of 1 mole of the crystal hydrate, ΔH_2.

Calculate the enthalpy of hydration of the anhydrous salt ΔH_{hydr}, taking into account the following considerations. The enthalpy of dissolution of the anhydrous salt ΔH_1 is the sum of enthalpies of hydration of the anhydrous salt ΔH_{hydr} and of dissolution of the

obtained crystal hydrate ΔH_2. The process of hydration and dissolution of the formed crystal hydrate can be expressed by two thermochemical equations (for example, for $Na_2CO_3 \cdot 10H_2O$):

$Na_2CO_3 + 10H_2O = Na_2CO_3 \cdot 10H_2O$; ΔH_{hydr}

$Na_2CO_3 \cdot 10H_2O + xH_2O = Na_2CO_3(x+10)H_2O$; ΔH_2

According to the Hess law

$$\Delta H_1 = \Delta H_{hydr} + \Delta H_2$$

Calculate ΔH°_{hydr} of the anhydrous salt, compare the results with those tabulated below, and determine the error.

Crystal hydrate	ΔH°_{hydr}, kJ/mol	Crystal hydrate	ΔH°_{hydr}, kJ/mol
$Na_2CO_3 \cdot 10H_2O$	−91.2	$SrCl_2 \cdot 6H_2O$	−78.7
$ZnSO_4 \cdot 7H_2O$	−95.0	$Na_2SO_4 \cdot 10H_2O$	−80.5

EXPERIMENT 9. ENTHALPY OF NEUTRALIZATION*

Determine the enthalpies of neutralization of hydrochloric and nitric acids with sodium and potassium hydroxide solutions and compare the four results.

Procedure. Place 50 ml of a 1 *N* acid solution into the inner beaker of a calorimeter and put the beaker into the calorimeter. Use another graduated cylinder to measure out 50 ml of a 1 *N* alkali solution and transfer the alkali into another beaker. Put the beaker next to the calorimeter for 3-4 minutes so that the temperature of the solution might be equalized with that inside the calorimeter. Measure the initial temperature of the calorimeter, and pour the alkali into the acid through the funnel with stirring: carry out the experiment as described on page 51.

Using Eq. (2) calculate the amount of heat liberated in the calorimeter during neutralization of the solutions. This amount of heat refers to neutralization of 0.05 mole of acid. Calculate the enthalpy of neutralization for 1 mole, in kJ/mol. Compare the results obtained by all other students and calculate the mean value. Compare it with the tabulated value of enthalpy of neutralization which is equal to −57.22 kJ per 1 mole of H_2O. Each student should determine the relative error of determination.

* The described experiment can only be used to determine the enthalpy of neutralization of strong acids with strong bases in dilute solutions because it does not depend on their nature but depends on the reaction

$H^+ + OH^- = H_2O$ (liquid) $\Delta H^\circ_{298} = -57.22$ kJ/mol

The enthalpy of neutralization of weak acids and bases is lower because energy is consumed during ionization of the acid and base.

EXPERIMENT 10. ENTHALPY OF SALT FORMATION

The enthalpy of formation of $MgSO_4$ ΔH°_{form} can be calculated from the following three equations using the Hess law:

$Mg(c) + H_2SO_4(aq) = MgSO_4(aq) + H_2(g)$; ΔH_1

$H_2(g) + S(rhomb) + 2O_2(g) + aq = H_2SO_4(aq)$; ΔH_2

$MgSO_4(aq) = MgSO_4(c) + aq$; ΔH_3

$Mg(c) + S\ (rhomb) + 2O_2(g) = MgSO_4(c)$; $\Delta H^\circ_{form} = \Delta H_1 + \Delta H_2 + \Delta H_3$

The enthalpy of dissolution of magnesium ΔH_1 and of its anhydrous sulphate in dilute sulphuric acid ΔH_3 should be determined experimentally, while the enthalpy of formation of a 0.1 *N* sulphuric acid solution ΔH_2 should be found in a reference book (—811.6 kJ/mol).

Procedure. Place 100 ml of a 0.1 *N* sulphuric acid solution into the reaction beaker and determine the initial temperature of the calorimeter. Weigh out a piece of magnesium of about 0.1-0.2 g to an accuracy of 0.02 g on a chemical balance and drop it into the acid with stirring. Carry out the experiment as described on page 51. Calculate ΔH_1. Determine ΔH_3 in a similar way by dissolving 1.5-2 g of anhydrous magnesium sulphate in the same sulphuric acid.

Calculate ΔH_1 and ΔH_3 from the experimental findings using formulas (2) and (3).

Calculate the enthalpy of formation of $MgSO_4$ by summing up the values of ΔH_1, ΔH_2, and ΔH_3 and compare with the reference value of —1278.8 kJ/mol in order to determine the experiment error.

Note: If time is limited, magnesium and its anhydrous sulphate can be dissolved by two students; when calculations are performed, then results are combined. The procedure of magnesium metal dissolution can be omitted at all, and the enthalpy of its dissolution may be taken from a reference table: $\Delta H_1 = -400.32$ kJ/mol.

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6 Solutions. Electrolytic Dissociation

QUESTIONS AND PROBLEMS

1. 500 ml of a 28% ammonia solution (density 0.9 g/cm^3) were diluted with 1 litre of water. Determine the concentration (in mass per cent) and molarity of the resultant ammonia solution.
Answer: 8.69%; 4.9 *M*.
2. What volume of water should be added to 500 ml of a 40% nitric acid (density 1.25 g/cm^3) in order to obtain a 10% acid solution? What will be the molar concentration of the obtained solution?

Answer: 1.88 l; about 0.17 *M*.

3. Mixed were 2 litres of a 60% sulphuric acid solution (density 1.5 g/cm³) and 3 litres of a 14% solution of the same acid (density 1.1 g/cm³). Determine the concentration (in per cent) of the resultant acid solution.
Answer: 35.9%.

4. What amounts of substances should be taken to prepare the following solutions:
(a) 2 litres of a 0.5 *M* solution of $AlCl_3$;
(b) 2 litres of a 0.5 *N* solution of $AlCl_3$;
(c) 400 ml of a 0.2 *M* solution of Na_2CO_3 from $Na_2CO_3 \cdot 10H_2O$;
(d) 400 ml of a 0.2 *N* solution of Na_2CO_3 from $Na_2CO_3 \cdot 10H_2O$?
Answer: (a) 135.5 g; (b) 44.5 g; (c) 22.88 g; (d) 11.44 g.

5. Determine molarity and normality of:
(a) a 70% solution of H_2SO_4, density 1.6 g/cm³;
(b) a 40% solution of NaOH, density 1.4 g/cm³;
(c) a 20% solution of H_3PO_4, density 1.1 g/cm³.
Answer: (a) 11.6 *M*, 23.2 *N*; (b) 14.4 *M*, 14.4 *N*; (c) 2.3 *M*, 6.9 *N*.

6. Determine concentration (in per cent) of the following:
(a) 4.9 *N* H_2SO_4 solution, density 1.15 g/cm³;
(b) 0.9*M* HNO_3 solution, density 1.03 g/cm³;
(c) a 4 *N* solution of $Cr_2(SO_4)_3$, density 1.21 g/cm³.
Answer: (a) 20.9%; (b) 5.5%; (c) 21.6%.

7. Two litres of a solution contain 0.1 mole of a weak binary electrolyte. Of this amount, 0.004 mole is in the form of ions. Determine the dissociation constant, the degree of dissociation, and the isotonic coefficient.
Answer: $K = 8.3 \times 10^{-5}$; $\alpha = 4\%$; $i = 1.04$.

8. The dissociation constant of formic acid at 18°C is 1.8×10^{-4}. Determine the degree of HCOOH dissociation at this temperature and the hydrogen ion concentration in a 0.04 *N* solution. Express the hydrogen ion concentration in mol/l and in g/ml.
Answer: $\alpha = 6.7\%$; $[H^+] = 2.68 \times 10^{-3}$ mol/l, or 2.68×10^{-6} g/ml.

9. Determine the isotonic coefficient and concentration of the NO_3^- ions (in mol/l and in g/l) in a 0.04 *N* solution of $Mg(NO_3)_2$ if the apparent degree of dissociation of the salt is 64%.
Answer: $i = 2.28$; $[NO_3^-] = 0.0256$ mol/l or 1.59 g/l.

10. Calculate the concentration of Na_2SO_4 in a solution (in mol/l and g/l), if the apparent degree of dissociation is 70% and the Na^+ ion concentration is 0.644 g/l.
Answer: 0.02 mol/l; 2.84 g/l.

11. Determine the chloride and calcium ion concentration in a 0.3 *N* solution of calcium chloride (in mol/l and in g/ml). The dissociation degree of the salt is 70%.
Answer: $[Ca^{2+}] = 0.105$ mol/l or 0.0042 g/ml; $[Cl^-] = 0.21$ mol/l or 0.0075 g/ml.

12. 60 g of a non-electrolyte were dissolved in 1500 g of water. The solution freezes at —1.86°C. What is the mass of 1 mole of the solute? ($K_{cr}^{H_2O} = 1.86$°C).
Answer: 40 g.

13. When 0.1 mole of a substance is dissolved in 5 litres of water, the boiling point of the solution rises by 0.016°C. Prove that the dissolved substance is an electrolyte ($K_{eb}^{H_2O} = 0.52$°C).

14. A litre of a solution contains 0.01 mole of sodium chloride. The osmotic pressure of this solution at 0°C is 0.428 atm. By how many times is this pressure higher than the osmotic pressure of a sugar solution of the same molarity? Determine the apparent degree of dissociation of the salt.
Answer: 1.9 times; 91%.

15. Determine the boiling point of ammonium chloride solution if 200 g of water contains 1.07 g of the solute (NH_4Cl). The dissociation degree should be assumed to be 80% ($K_{eb}^{H_2O} = 0.52°C$).
Answer: 100.09°C.
16. 0.71 g of Na_2SO_4 was dissolved in 500 ml of water. Determine the freezing point of the solution. Assume the dissociation degree of Na_2SO_4 to be 70% ($K_{cr}^{H_2O} = 1.86°C$).
Answer: —0.04°C.
17. Determine the molar concentration of a binary electrolyte if its aqueous solution starts freezing at —0.298°C and the apparent degree of dissociation is 60 per cent.
Answer: 0.1 *M*.
18. Write the expressions for the constants of dissociation of carbonic acid (K_1 and K_2). Which of these two values is less? Why?
19. How can the following salts be converted into normal ones:
(a) Na_2HPO_4; (b) $Al(OH)_2Cl$; (c) $NaHCO_3$; (d) $(MgOH)_2CO_3$?
Write down the ionic equations for the corresponding reactions bearing in mind that the basic salts are sparingly soluble.
20. Substances given below were mixed in pairs

(a) $NaClO + CH_3COOH$
(b) $NaCl + CH_3COOH$
(c) $NaCl + KOH$
(d) $MgCl_2 + KOH$
(e) $NaH_2PO_4 + Na_3PO_4$
(f) $NaHSO_4 + Na_2SO_4$
(g) $Na_2SO_4 + NaOH$
(h) $NaHSO_4 + NaOH$

Which of these reactions are exchange ones? Write down the ionic equations for possible reactions.
21. A solution contains a mixture of salts: $AgNO_3$, $Ba(NO_3)_2$ and $Zn(CH_3COO)_2$. Excess hydrochloric acid is added. Write down the ionic equations for possible reactions.
22. Mixed were solutions of Na_2S, $Ba(NO_3)_2$ and excess H_2SO_4. What reactions will take place? Write down the ionic equations for these reactions.
23. Write down the equations for stepwise dissociation of hydrosulphuric acid. In what direction will these equilibria be shifted if HCl or NaOH is added?
24. To neutralize 20 ml of a sulphuric acid solution 25 ml of a 0.05 *N* solution of NaOH were spent. Determine the normality and the titre of the sulphuric acid solution.
Answer: 0.06 *N*; 0.003 g/ml.
25. What volume of a 1 *N* alkali solution is needed to neutralize 10 ml of a 10% solution of nitric acid having the density of 1.056 g/cm³?
Answer: 167.77 ml.
26. To neutralize 25 ml of hydrochloric acid of unknown concentration, 30 ml of a 0.1 *N* solution of NaOH were spent. Calculate the normality, molarity and the titre of the hydrochloric acid solution.
Answer: 0.12 *N*; 0.12 *M*; 4.38×10^{-3} g/ml.
27. 0.01575 g of oxalic acid $H_2C_2O_4 \cdot 2H_2O$ was spent to neutralize 25 ml of NaOH solution. Determine the normality, molarity and the titre of the sodium hydroxide solution.
Answer: 0.01 *N*; 0.01 *M*; 0.0004 g/ml.
28. To precipitate iron(III) hydroxide from 15 ml of ferric chloride solution, 10 ml of a 0.1 *N* NaOH solution were spent. Calculate the concentration of Fe^{3+} ion in the test solution (in mol/l and g/l).
Answer: 0.022 mol/l; 1.241 g/l.
29. Iodine was extracted from 20 ml of iodine water containing 0.3 g iodine by two methods: (a) by adding 2 ml of amyl alcohol at a time, and (b) adding alcohol in two 1-ml portions with complete removal of the alcoholic solution of iodine after the first extraction.

Calculate the concentration of non-extracted iodine (in % of its initial content in iodine water) after a one- and two-step extraction. The coefficient of iodine distribution between amyl alcohol and water $K = c_{I_2 \text{ in alcohol}}/c_{I_2 \text{ in water}} = 233$. Which method is more effective?
Answer: (a) 4%; (b) 2%.

Examples of Multiple-choice Questions

1. What is the normality of a 40% solution of sulphuric acid having the density of 1.3 g/cm³?
(1) 10.4; (2) 46.4; (3) 23.2; (4) 11.6; (5) 20.8.
2. What volume (in ml) of a 0.8 *N* KOH solution is needed to neutralize 24 ml of a 0.2 *N* solution of HCl?
(1) 3; (2) 12; (3) 6; (4) 18; (5) 24.
3. What is the value of the isotonic coefficient of K_2SO_4 solution, if the apparent degree of dissociation $\alpha = 60\%$?
(1) 6; (2) 2.2; (3) 1.2; (4) 4.4; (5) 0.6.
4. What is the chloride ion concentration (in mol/l) in a 0.05 *M* solution of $AlCl_3$, if its dissociation degree $\alpha = 80\%$?
(1) 0.05; (2) 0.1; (3) 0.4; (4) 0.12; (5) 0.24.
5. What is the freezing point of a solution containing 0.005 mole of Na_2CO_3 in 100 g of H_2O, if its apparent degree of dissociation $\alpha = 0.53\%$?
(1) −2.93; (2) −0.28; (3) −0.093; (4) −1.86; (5) −0.186.

EXPERIMENT 11. PREPARING SOLUTIONS. SOLUBILITY

Apparatus and reagents

Chemical balance with a set of weights. Drying cabinet. Set of hydrometers. Thermometers (100 and 150 °C). Graduated cylinders, 50-, 25-, 15- and 10-ml. Conical flasks, 50-ml. Volumetric flasks, 50- and 100-ml. Flat-bottomed flask, 200-250-ml. Weighing bottle, diameter 50 mm. Pipette, 3- and 5-ml. Burette, 100-ml. Funnel, diameter 30 and 40 mm. Test tube, 10-12-ml, diameter 20 mm. Beakers, 50- and 100-ml. Forceps. Desiccator. Sodium hydroxide. Potassium dichromate. Sulphuric acid, 10-15% solution. Sodium hydroxide: 5% and 30% solutions.

Determining the density of a solution. The density ρ of a solution depends on the concentration of the solute. This dependence has been determined for common acids, soluble bases and salts and is given in reference books and tables (see Table 4 of the Appendix). Therefore the concentration of a solute can tentatively be determined (to an accuracy of ±0.5%) by measuring the density of a solution, with subsequent reference to the table of concentrations and densities.

The density of solutions is usually determined by a hydrometer. To do so, the test solution is placed in a glass cylinder and various hydrometers are then tried until a hydrometer is found whose scale is suitable for reading the liquid level. The hydrometer should not

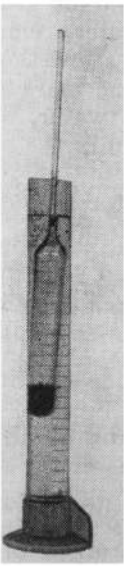


Fig. 33.
Hydrometer

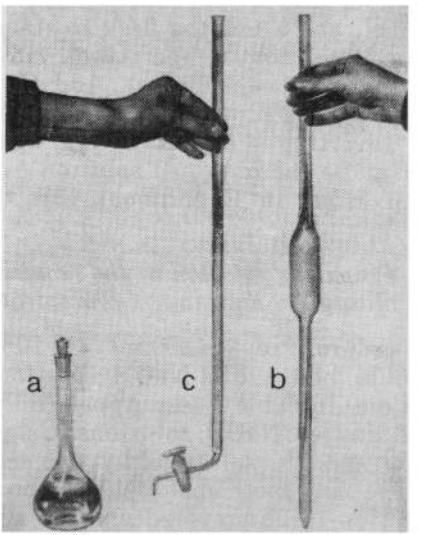


Fig. 34.
Volumetric (measuring) vessels:
a–measuring (volumetric) flask;
b–pipette; *c*–burette

touch the cylinder walls as shown in Fig. 33. The scale of a hydrometer re ads the liquid level in units of density to an accuracy of the third decimal place.

More accurate determination of concentration of a solute should be done by methods of analytical chemistry.

1. Preparing Solutions of Various Concentrations

A. Preparing 0.1 M and 0.1 N solutions of sulphuric acid

Procedure. Place 10-15% sulphuric acid into a glass cylinder and dtetrmine its density using a hydrometer as shown in Fig. 33. What coneentration of H_2SO_4 (in %) corresponds to the found density of he cacid? (Consult the Appendix, Table 4).

Calculate the volume of this acid which is necessary to prepare 100 ml of sulphuric acid of the required concentration (0.1 *M* or 0.1 *N*, as asked by the instructor). Measure out this volume using a graduated cylinder of 10-15 ml capacity.

Fill a 100-ml volumetric flask (Fig. 34*a*) with distilled water from a wash bottle to about 1/4 its capacity. Stir the liquid in the flask

by circular movement and add slowly the acid from the graduated cylinder through a funnel. Rinse the funnel with water, remove the funnel, and allow the flask to stand for a while (to allow the liquid to cool to room temperature). Now add water to the mark (by the bottom of the meniscus). Add the last portions of water, drop by drop, from a pipette. Stopper the flask tightly and mix the solution by inverting the flask several times.

Handle the obtained solution over to the instructor (it should be used later, in Experiment 12).

B. Preparing solution of the required concentration by mixing solution of higher and lower concentrations

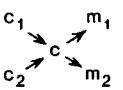
Procedure. Prepare 200 ml of a 10% sodium hydroxide solution from a 30% and a 5% NaOH solutions*.

Consult Table 4 (see Appendix) to find the densities of the initial and desired NaOH solutions. Calculate the volumes of the starting 30% and 5% solutions by two methods.

The first method. Calculate the mass of 200 ml of a 10% NaOH solution to be prepared and the mass of NaOH contained in it. Let the volume of the 30% solution be designated by X ml and of the 5% solution by Y ml. Make up the equations for calculation of the masses of the starting NaOH solutions and the masses of NaOH contained in them.

We have two equations with two unknowns. In the first one the sum of masses of the starting solutions is equated to the mass of the required solution, and in the second, the summary masses of NaOH in the initial solutions are equated to the mass of NaOH in the wanted solution. Solve this system of equations to find X and Y which are the volumes in ml of the 30% and 5% solutions required to prepare 200 ml of the 10% alkali solution.

The second method. This method employs the so-called "cross" rule:



where c is the sought concentration, %; c_1 and c_2 are the higher and the lower concentrations of the initial solutions (for pure water $c_2 = 0$), respectively, %; m_1 and m_2 are masses of the initial solutions of higher and lower concentrations. Thus, $m_1 = c - c_2$; $m_2 = c_1 - c$.

* Any other substance can be used instead of sodium hydroxide (as may be indicated by the instructor).

Using the "cross" rule calculate the masses of the starting 30% and 5% solutions. Consult the table of densities and find the volumes of solutions (in ml).

The results of calculations performed by the two methods should not differ by more than ±1 ml.

Measure out the calculated volumes of the starting solutions, pour them into a 200-ml flask, close the flask with a stopper and mix thoroughly by overturning the flask several times. Transfer a portion of the obtained solution into a cylinder and measure its density using a hydrometer. Find the concentration (in %) of the obtained solution from Table 4 (see Appendix). Write down all calculations into the log-book, the density of the prepared solution and its per cent concentration, as found in Table 4. Establish the deviation of the concentration obtained experimentally from the calculated one.

2. Determining Solubility of Potassium Dichromate

Procedure. Weigh out about 2 g of powdered potassium dichromate $K_2Cr_2O_7$ on a chemical balance and transfer into a 50-ml beaker. Add 10 ml of distilled water. Put the beaker on a gauze over a burner and heat to complete dissolution of the salt. Cool the clear solution to room temperature.

What happens as the solution cools? Explain your observations.

When all the crystals precipitate to the bottom and the supernatant solution is absolutely clear, rinse a wide 10-ml test tube with about 2 ml of the supernatant solution, discard this portion, and then carefully transfer the supernatant solution into the test tube not allowing crystals to enter it. Measure the temperature of the solution.

Can this solution be regarded as saturated at this temperature?

Weigh a weighing bottle on a chemical balance. Place 3 ml of the prepared $K_2Cr_2O_7$ solution using a burette (Fig. 34*c*). Weigh the bottle with the solution and put into a drying cabinet. Keep the solution in the cabinet at a temperature of about 90°C to remove all water. Raise the temperature to 150°C and dry the salt for 30 minutes. Cool the weighing bottle with the salt in a desiccator to room temperature and weigh. Repeat drying at 150°C for 10 minutes and weigh again. The determination can be considered finished when the results of two successive weighings do not differ by more than 0.02 g.

Recording the results and calculations. Write down the results of the experiment as shown below:

Temperature of saturated solution, t, °C.

Volume of saturated solution taken for the determination of solubility, V, ml.

Mass of weighing bottle, m_1, g.

Mass of weighing bottle with the solution, m_2, g.

Mass of dichromate solution, $m_3 = m_2 - m_1$, g.

Mass of weighing bottle with dry salt, m_4, g (1st weighing, m_4', g; 2nd weighing, m_4'', g).

Weight of dry dichromate, $m_5 = m_4 - m_1$, g.

Use the results to calculate the solubility (concentration of a saturated solution) of potassium dichromate, in % and in g/100 g of H_2O. Compare the obtained value with the data given in Table 5 of the Appendix.

EXPERIMENT 12. DETERMINING CONCENTRATION OF SOLUTIONS BY TITRATION

Apparatus and reagents	
Pipettes, 3-, 5-, and 15-ml.	Erlenmeyer flasks, 30-50 ml. Watch glass.
Burette, 10-ml.	Iodine, crystals. Amyl alcohol. Methyl orange. Solutions: sodium hydroxide, 0.1 *N*, standard; sodium thiosulphate, 0.05 *N*, standard; starch.
Graduated cylinders, 25- and 50-ml.	

The concentration of a solution can easily be calculated if the volumes of solutions of two reactants are accurately measured, and the concentration of one solution is known. The process of gradual addition of a standard solution (titrant) of known concentration to an accurately measured volume of the solution with unknown concentration (titrand) or vice versa is known as titration.

1. Determining Acid Concentration

Procedure. The concentration of sulphuric acid prepared in Experiment 11 (part 1*A*) should be determined. If this experiment was not carried out, obtain the acid from the instructor. Obtain also a 0.1 *N* solution of alkali, whose concentration is known (standard solution), and methyl orange indicator.

Fill a test tube with a 2 *N* sulphuric acid solution to 1/3 its capacity, and place an equal volume of a 2 *N* alkali solution into another test tube. Add a drop of methyl orange into each test tube and observe the colour change in the acid and alkali.

Rinse a 10-ml burette (Fig. 34*c*) with a small volume of the acid and discard the acid through the tap in the bottom. Fix the burette in a stand and fill with the acid through a funnel to the level slightly above zero. The tip of the burette should be filled with the acid. Adjust the liquid level in the burette to zero by discharging the acid, drop by drop, through its lower end. Read the level by the bottom of the meniscus.

Using a dry pipette transfer 3 ml of the standard solution of sodium hydroxide into a 30-50 ml Erlenmeyer flask and add a small quantity of water from a wash bottle to dilute the solution to 8-10 ml. Now add a drop of methyl orange and carry out a tentative experiment. To do this, add the acid by small (0.5-ml) portions from a burette until the colour of methyl orange changes. During the experiment, stir the flask contents continually by circular movements. Stop adding the acid at the moment when the indicator colour changes. Calculate the amount of the acid spent in this procedure to an accuracy of tenth fractions of a millilitre.

Repeat the titration three times but to a higher accuracy. To that end, the last portions of the acid (0.5-0.7 ml) should be added drop by drop. A vivid colour change from addition of a drop of the acid indicates the point of equivalence (termination of the reaction). Determine the volume of spent acid to an accuracy of hundredth fractions of a millilitre.

The flask for the alkali should be washed and rinsed with distilled water before each titration and the liquid level in the burette should be set to zero.

Recording the results and calculations. Write down the molecular and ionic equations for the reaction. Record the results in the following form:

Nos.	Volume of a 0.1 *N* alkali solution, ml	Methyl orange indicator, number of drops	Volume of acid spent for titration, ml
1	3	1	3.26
2	3	1	3.24
3	3	1	3.25
			mean 3.25

Determine the arithmetic mean of the last three titration results which differ by not more than 0.05 ml. Since the number of equivalents of the acid that reacts with the alkali is equal to the number of equivalents of the alkali taken, the normality of the acid can be found from the equations $V_{acid}N_{acid} = V_{alk}N_{alk}$. Calculate also the molarity and the titre (i.e. the number of grams in 1 ml of solution) of the acid.

2. Determining Coefficient of Iodine Distribution between Amyl Alcohol and Water

Procedure. Using a graduated cylinder, measure out 50 ml of distilled water and 25 ml of amyl alcohol* into a cylinder fitted with

* Any other substance that dissolves iodine and is immiscible with water can be used. These may be benzene, petrol, carbon tetrachloride, etc.

a ground-glass stopper. Weigh out 0.5 g of iodine on a watch glass using a chemical balance and transfer it into the cylinder. Close the cylinder with the stopper and shake energetically by inverting the cylinder for five minutes. Allow the cylinder to stand for a few minutes until complete separation of the aqueous and alcoholic solutions occurs.

In the meantime, place a 0.05 *N* standard solution of sodium thiosulphate $Na_2S_2O_3$ into a burette, 3-4 cm above the zero reading. Place an empty beaker beneath the burette. Be careful that the burette tip is filled with the solution (air bubbles should be absent), and let the solution out until the bottom of the meniscus reaches zero.

After complete separation of the layers, transfer by a pipette 5 ml of the alcoholic solution of iodine from the upper layer into an Erlenmeyer flask (the pipette end should be above the interface of the two phases) and add 5 ml of distilled water from a graduated cylinder. Shake the contents of the Erlenmeyer flask and add 3-4 drops of sodium thiosulphate from a burette until the intense colour of the alcoholic solution changes to pale pink. Now add 1 ml of starch solution: the solution turns blue. Continue titration until the solution is completely colourless. Write down into the log-book the volume of the thiosulphate solution used for titration of the first sample of the alcoholic iodine solution. The reaction proceeds according to this equation

$$\underset{\text{(colourless)}}{2Na_2S_2O_3} + \underset{\text{(coloured)}}{I_2} = \underset{\text{(colourless)}}{2NaI} + \underset{\text{(colourless)}}{Na_2S_4O_6}$$

Using a dry pipette, transfer 15 ml of the aqueous solution of iodine from the lower layer into another Erlenmeyer flask. In order to prevent penetration of the alcoholic solution into the pipette as it passes the alcoholic layer, close the upper opening of the pipette with the finger tip and open it only after the pipette end is 1-2 cm below the interface. Add 1 ml of starch solution to the Erlenmeyer flask: the solution turns blue again. Titrate carefully with the sodium thiosulphate solution until the blue colour vanishes. Write down into the log-book the volume of the thiosulphate solution spent for titration of the first sample of the aqueous solution of iodine.

Close the cylinder with the stopper again and shake its contents for another 2-3 minutes. Allow the mixture to stand and separate into layers and take samples of each layer again. Repeat the titration with sodium thiosulphate solution.

Recording the results. Calculate the coefficient of iodine distribution between amyl alcohol and water. Write down the results of

your calculations into the following table:

Solution	Sample No.	Volume of iodine solution (pipette), ml	Volume of thiosulphate solution spent for titration, ml	Normality of iodine solution	Iodine concentration, g/l
Alcoholic	1 2				
Aqueous	1 2				

The distribution coefficient K is equal to the ratio of concentration of the solute in the first solvent to that in the second solvent: $K = c_1/c_2$, where c_1 and c_2 are usually expressed in g/l.

Calculate the normality of iodine solution N_{I_2} in each sample by the following equation:

$$V_{I_2}N_{I_2} = V_{Na_2S_2O_3}N_{Na_2S_2O_3}$$

Express the iodine concentration c_{I_2} in each sample in g/l. To do so, multiply normality of the iodine solution by mole equiv. of iodine, which is 126.9 g. Calculate the distribution coefficient $K = c_{I_2 \text{ in alcohol}}/c_{I_2 \text{ in water}}$ for the first and second samples. How many times is the solubility of iodine in amyl alcohol higher than in water?

3. Extracting Iodine from Aqueous Solution with Amyl Alcohol

Procedure. Place 20 ml of iodine water and 2 ml of amyl alcohol into a cylinder. Stopper the cylinder and shake energetically for 2-3 minutes. Allow the mixture to stand for separation. How has the colour intensity of the aqueous iodine solution changed after shaking with amyl alcohol? What is the colour of the alcoholic iodine? Using a pipette, collect the upper layer of alcoholic iodine solution. Remove the remaining alcoholic iodine solution from the surface of the aqueous solution by filter paper. Transfer about 2 ml of the aqueous solution into a test tube, add 10 drops of starch solution, shake the mixture, and note the intensity of the blue colour.

Repeat the iodine extraction from 20 ml of iodine water with the same amount (2 ml) of amyl alcohol but adding it in four steps (in 0.5-ml portions). Shake the mixture energetically after adding each new portion of amyl alcohol, allow the mixture to separate and remove the alcoholic layer from the surface of aqueous solution with filter paper. After the fourth portion of the alcoholic solution

is removed, transfer about 2 ml of the aqueous solution into a clean test tube and add 10 drops of starch. Compare intensities of the blue colour of the aqueous solutions after the first and second stage.

Recording the results. Write down in the log-book the conditions of the experiments. Analyze your observations to conclude on the efficiency of the one- and four-step extraction of iodine.

EXPERIMENT 13. ELECTROLYTIC DISSOCIATION

Apparatus and reagents	
Apparatus for comparing electric conductivity of solutions. Beaker, 50-ml. Sugar (powder). Sodium chloride. Marble (crushed). Sodium acetate. Ammonium chloride. Zinc. Litmus paper. Methyl orange. Phenolphthalein. Solutions:	hydrochloric acid, 2 *N*, 0.1 *N* and 0.5 *N*; acetic acid, 2 *N* and 0.1 *N*; sodium hydroxide, 2 *N*, 0.1 *N* and 0.5 *N*; ammonium hydroxide, 2 *N* and 0.1 *N*; magnesium sulphate, 0.5 *N*; sodium silicate, 0.5 *N*; aluminium chloride, 0.5 *N*; nickel sulphate, 0.5 *N*; zinc sulphate, 0.5 *N*.

1. Comparing Electric Conductivity of Solutions of Some Electrolytes

Procedure. Lower carbon electrodes fixed in a wooden board into a 50-ml beaker and connect them in series with the bulb (Fig. 35). Actuate the circuit.

Pour 20-30 ml of distilled water into the beaker. Will the bulb light up? Does distilled water conduct electricity?

Add 4-5 microspatulas of powdered sugar. Does sugar solution conduct electricity? Transfer the electrodes into a beaker with distilled water and rinse them. (Disconnect the apparatus from the mains each time before removing the electrodes from the beaker.)

Place common salt into a dry beaker to cover the bottom and immerse the electrodes into the salt. Does dry salt conduct electric current? Add 20-30 ml of distilled water from a wash bottle and observe the bulb. Rinse the electrodes in the beaker containing distilled water.

Explain why salt solutions conduct electricity while distilled water and dry salt taken separately do not.

Place 20-30-ml portions of a 0.1 *N* solutions of hydrochloric acid, sodium hydroxide, acetic acid and ammonia solution into four separate 50-ml beakers. Test the solutions for electric conductivity by immersing the electrodes into them and passing electric current. Each time rinse the electrodes with distilled water. Note the different brightness of the bulb, and from this conclude on the strength of the acids and bases.

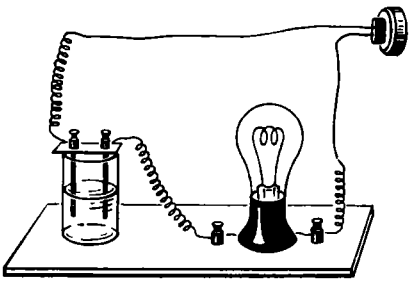


Fig. 35.
Set-up for measuring conductivity of solutions

Mix the solutions of acetic acid and ammonium hydroxide and test the resultant solution for conductivity. Explain the different brightness of the bulb as electric current passes through the solutions of acetic acid and ammonium hydroxide taken separately and through their mixture.

Describe your observations and explain them.

2. Dissociation of Hydroxides

Procedure. Label five test tubes and place 4-5 drops of the following 0.5 *N* solutions: $MgCl_2$ into test tube No. 1, $AlCl_3$ into test tube No. 2, Na_2SiO_3 into test tube No. 3, $NiSO_4$ into test tube No. 4, and $ZnSO_4$ into test tube No. 5. Add a few drops of a 0.5 *N* alkali solution into test tubes Nos. 1, 2, 4 and 5 (until precipitation of the hydroxides begins), and of a 2 *N* solution of hydrochloric acid into test tube No. 3. Determine the chemical character of the precipitated hydroxides. Transfer about half volume of magnesium hydroxide suspension from test tube No. 1 into a clean test tube and add 4-5 drops of a 0.5 *N* HCl solution; add 6-8 drops of a 0.5 *N* alkali solution to the remainder in test tube No. 1. In which test tube does magnesium hydroxide dissolve? Has $Mg(OH)_2$ acidic, basic, or amphoteric properties?

Using the same procedure, test the properties of the hydroxides of aluminium, silicon, nickel(II) and zinc. In what solutions can they be dissolved? What are their chemical properties?

Recording the results and discussion of some factors important for the character of dissociation of hydroxides.

1. Fill in the following table to characterize hydroxides of magnesium, aluminium, and silicon:

Hydroxide	Chemical properties	Formula	Dissociation equation (without steps)
Magnesium hydroxide Aluminium hydroxide Silicon hydroxide			

How many electrons are in the outer shell of the ions Mg^{2+}, Al^{3+} and the silicon atom in the oxidation state of +IV? How do the acid properties of the hydroxides change (increase or decrease) with increasing charge of the ion (oxidation state of atoms)?

The radii of the Mg^{2+}, Al^{3+} and the silicon atom in the oxidation state of +IV are, according to Pauling, 0.065, 0.050 and 0.041 nm, respectively. How do the chemical properties of their hydroxides depend on the ion radius?

2. Compile the second table using the data characterizing dissociation of hydroxides of magnesium, nickel, and zinc, in which the ions of the elements bear the same charge and have about the same radii.

Ion forming the hydroxide	Ionic radius, nm	Outer electron shell of ions	Chemical properties of hydroxides	Dissociation equation (without steps)
Mg^{2+}	0.065			
Ni^{2+}	0.069			
Zn^{2+}	0.071			

How does the character of dissociation of the hydroxides depend on the structure of the outer shell of the ions, if it is known that $Mg(OH)_2$ is a stronger base than $Ni(OH)_2$?

Make general conclusion about the dependence of hydroxide dissociation on the ion radius, charge, and the structure of the outer electron shell.

When writing down the equations for dissociation of amphoteric hydroxides, take into account that they convert into hydroxocomplexes in aqueous alkaline solutions. For example, dissociation equation of the amphoteric zinc hydroxide can be written as follows:

$$2OH^- + Zn(H_2O)_4^{2+} \underset{\text{in acidic solution}}{\rightleftarrows} Zn(OH)_2 + 4H_2O \underset{\text{in alkaline solution}}{\rightleftarrows} [Zn(OH)_4]^{2-} + 2H_3O^+$$

Write down the equation for dissolution of $Zn(OH)_2$ and $Al(OH)_3$ in acid and alkali.

3. Comparison of Chemical Activity of Acids

A. Reactions of hydrochloric and acetic acids with marble

Procedure. Place 3-4 drops of a 2 *N* acetic acid into one test tube and the same amount of a 2 *N* hydrochloric acid into another test tube. Take two pieces of marble of about the same size and drop one into each test tube. What gas is liberated?

Recording the results. In which test tube is the reaction more vigorous? Write down the molecular and ionic equations for the reactions. Concentration of which ions influences the rate of gas liberation? The hydrogen ion concentration is higher in which acid?

Derive your conclusion about the relative strength of the acids in question.

B. Reactions of hydrochloric and acetic acids with zinc

Procedure. Place a 2 *N* solution of hydrochloric acid and a 2 *N* solution of acetic acid into two separate test tubes to 1/3 their capacity. Take two pieces of zinc of about the same size and place one into each test tube.

Recording the results. In which test tube is the liberation of hydrogen more energetic? Write down the ionic equations for the reactions. Explain your observations (the different reaction rates).

4. Shifting Equilibrium of Dissociation of Weak Electrolytes

A. Effect of salt of weak acid on dissociation of this acid

Procedure. Place 5-7 drops of a 0.1 *N* acetic acid solution into each of the two test tubes. Add a drop of methyl orange to each solution. What ions change the colour of the indicator to pink? Keep one test tube as a reference and add 3-4 microspatulas of sodium acetate into the other solution. Stir the salt using a glass rod. Compare the colour of the obtained solution with the colour of the reference solution. The change of colour of methyl orange indicates the change in the concentration of which ions?

Recording the results. Write down the equation for dissociation of acetic acid and the expression of its dissociation constant. Explain the shift of the equilibrium of the acid dissociation as sodium acetate is added to it. How does the degree of dissociation of acetic acid and the hydrogen ion concentration change?

B. Effect of salt of weak base on dissociation of this base

Procedure. Place 5-7 drops of a 0.1 *N* ammonium hydroxide solution into each of the two test tubes. Add a drop of phenolphthalein solution into each test tube. Which ions turn phenolphthalein red?

Keep one test tube with the ammonium hydroxide for reference, and add 3-4 microspatulas of ammonium chloride into the other solution. Stir the mixture using a glass rod and compare the colour of the resultant solution with that of the reference solution.

Recording the results. Write down the equilibrium equation of ammonium hydroxide. How does the equilibrium in this solution shift when ammonium chloride is added? Why does the colour of phenolphthalein fade?

EXPERIMENT 14. DETERMINING DEGREE OF ELECTROLYTE DISSOCIATION

Apparatus and reagents

Chemical balance with a set of weights. Beakers, 100-ml. Graduated cylinder, 100-ml. Cryoscope. Pipettes, 10-ml. Circuit for measuring resistance of solutions (see footnote to 2). Ice. Snow. Sodium chloride, crystalline. Potassium chloride, crystals, and 0.02 *N* solution. Potassium iodide, crystals. Potassium nitrate, crystals. Sodium nitrate, crystals. Acetic acid, 1 *N* solution.

1. Cryoscopic Determination of Apparent Degree of Dissociation of Strong Electrolytes

The degree of electrolyte dissociation can be determined by the deviation of the lowering of the crystallization point of electrolyte solution from the lowering of the crystallization point of a non-electrolyte of the same molal concentration.

Apparatus shown in Fig. 36 is used in the experiment. The outer beaker (500-ml) is filled with a mixture of ice or snow with table salt. A thermometer graduated in 0.1°C (a lower reading is —3°C, readings above zero do not matter) is installed in the inner 200-ml beaker. The beaker is also provided with a wire stirrer. Various readily soluble salts, e.g. NaCl, KCl, KI, KNO_3, or $NaNO_3$ can be taken for the experiment.

Procedure. Obtain a salt from the instructor and determine the degree of its dissociation as follows. Fill the space between the outer and inner beakers with a mixture of snow and common salt. Place 100 ml of distilled water in the inner beaker and assemble the apparatus. Determine the freezing (crystallization) point of pure water. (It can deviate slightly from 0°C because of inaccuracy of thermometer calibration.) Record the thermometer readings at 20-second intervals during 4 minutes, with stirring. Draw a curve showing the temperature drop with time (temperature should be plotted against the axis of ordinates). Point out on the curve the temperature at which the first crystals of ice appear. This is the crystallization point of water. Water can sometimes be supercooled, and as ice crystals appear, the temperature may slightly elevate but then drops again. In this case the crystallization point should be located on the curve after the temperature rise but before the second fall (examine

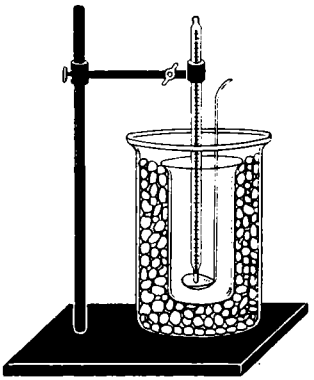


Fig. 36.
Cryoscope

the shape of your curve). Write down the crystallization point of pure water established by this procedure.

Weigh a dry beaker (200-ml) on a chemical balance and place the amount of salt obtained from the instructor corresponding to 0.2 mole. Weigh the beaker with the salt. Add 100 ml of distilled water and dissolve the salt. Determine the crystallization point of the solution as described above. The crystallization point should be determined at the moment of the appearance of the first crystals. Supercooling of the solution is also possible and it should be taken into consideration.

Recording the results and calculations. Write down your observations into the log-book. The results of measurements should be recorded as follows:

Mass of beaker, m_1, g.
Mass of beaker with salt, m_2, g.
Mass of salt, $m = m_2 - m_1$, g.
Mass of water, m_{H_2O}, g (equal numerically to its volume in ml).
Crystallization point of water, t_{cryst}, °C.
Crystallization point of solution, t'_{cryst}, °C.
Calculate the molal concentration of the solution c:

$$c = \frac{m \times 1000}{M m_{H_2O}}$$

where M is the molecular mass of the salt.

Calculate the lowering of crystallization point of a non-electrolyte solution using the Raoult law

$$\Delta t_{non\text{-}electr} = K_{H_2O} c$$

where K_{H_2O} is the cryoscopic constant of water (1.86°).

Determine the lowering of the crystallization point of the electrolyte Δt_{electr} from your experimental findings

$$\Delta t_{electr} = t_{cryst} - t'_{cryst}$$

Explain the difference between this value and the calculated value for the non-electrolyte solution.

Determine the isotonic coefficient:

$$i = \frac{\Delta t_{electr}}{\Delta t_{non\text{-}electr}}$$

The relationship between the isotonic coefficient and the dissociation degree α is expressed by the formula

$$\alpha = \frac{i-1}{n-1}$$

where n is the number of ions into which the electrolyte falls.

Since the salts in question are binary electrolytes, the apparent degree of dissociation can be calculated from this formula

$$\alpha = i - 1$$

Why is thus determined dissociation degree called apparent? How does it depend on the concentration of the salt?

Prove your answer to the last question experimentally by determining the freezing point of a decimolar solution of the salt. To do this, calculate the amounts of salt and water required to prepare a 0.1 N solution of this salt and determine its freezing point again.

2. Determining Degree and Constant of Dissociation of Weak Electrolyte by Measuring Its Electric Conductivity

The degree of dissociation of a weak electrolyte is connected with equivalent conductivity and ion mobility, which is expressed by the following formula

$$\lambda = \alpha (l_c + l_a) \qquad (1)$$

where λ is equivalent conductivity, Sm $\times$ cm^2/mol. equiv or Ohm^{-1} $\times$ cm^2·(mol. equiv)$^{-1}$; l_c is the cation mobility, Sm $\times$ cm^2, and l_a is the anion mobility, Sm $\times$ cm^2. But it is easier to determine experimentally not conductivity but resistance, which is expressed by the formula

$$R = \rho \frac{l}{s} \qquad (2)$$

where l is length, s cross sectional area of conductor, and ρ is specific resistance at $l = 1$ cm and $s = 1$ cm^2.

The value reciprocal of ρ is called specific conductance: $\varkappa = 1/\rho$; hence $R = l/\varkappa s$. Since l/s depends only on the electrode dimensions and the distance between them, specific conductance can be calculated by determining resistance of electrolyte experimentally.

Equivalent conductivity is related to the specific conductance $\varkappa$ and the solution concentration as follows:

$$\lambda = \varkappa V \tag{3}$$

where V is dilution or volume of solution, expressed in ml and containing an equivalent weight of the dissolved electrolyte.

It follows that

$$V = 1000/c$$

where c is normality of solution.

Equivalent conductivity can now be calculated from specific conductance using the following equation

$$\lambda = \frac{\varkappa \times 1000}{c} \tag{4}$$

Since the dissociation degree increases with dilution and nears unity, while the ion mobility remains practically unchanged, equivalent conductivity increases as well to attain its maximum λ_∞ in an infinitely diluted solution; therefore, $\lambda_\infty = l_c + l_a$ and $\lambda = \alpha\lambda_\infty$, whence

$$\alpha = \frac{\lambda}{\lambda_\infty} \tag{5}$$

It is necessary to determine the degree and constant of dissociation of acetic acid of various concentrations. The ion mobilities for CH_3COOH (disregarding their dependence on temperature) are

$$l_{H^+} = 315 \text{ Sm} \times \text{cm}^2 \quad l_{CH_3COO^-} = 36 \text{ Sm} \times \text{cm}^2$$

Hence

$$\lambda_\infty = 315 + 36 = 351 \text{ Sm} \times \text{cm}^2$$

Procedure. Any apparatus for measuring resistance of solution can be used.*

Before the student begins carrying out the experiment it is necessary to determine resistance R and l/s ratio which, at a given temperature, does not depend on the nature of the electrolyte or its concentration. In other words, it is a constant for a given vessel where resistance of solution will be determined. To do this, the vessel should be filled with a solution with known specific conductance, its resistance is measured, and l/s is found using Eq. (2). A 0.02 N potassium chloride solution is commonly used. A calibration graph showing the dependence of specific conductance on resistance should be plotted beforehand and kept by side of the apparatus for measuring resistance.

* A Wheatstone bridge can be used for the purpose.

Place 20 ml of a 1 N solution of acetic acid into a vessel and determine its resistance R. Find the corresponding specific conductance $\varkappa$ on the graph. Write down these values into a table (see below). Prepare two pipettes (10-ml): one for the solution and the other for water. Using a pipette, take 10 ml of the solution from the vessel and add 10 ml of water to the remaining 10 ml in the vessel using another pipette (intended for water). Stir thus prepared 0.5 N solution using the pipette and measure its resistance again. Repeat the determinations with 0.25 N, 0.125 N, 0.062 N, and 0.031 N solution (each time diluting the solution by half). Write down the obtained values of R and $\varkappa$ into the table.

Recording the results and calculations. Calculate equivalent conductivity λ for each concentration using Eq. (4), degree of dissociation using Eq. (5), and the dissociation constant:

$$K = \frac{\alpha^2}{V(1-\alpha)}$$

Write down the results of the experiment and calculations into the table:

Concentration of acid anions, c, mol. equiv/l	Resistance, R ohm	Specific conductance, $\varkappa$, ohm×cm^{-1} (from the calibration graph)	Equivalent conductivity, λ, ohm×cm^2/mol.equiv	Dissociation degree, α	Dissociation constant, K

Draw a graph showing the dependence of dissociation degree on solution concentration (in mol. equiv/l). How does the dissociation degree vary with concentration?

Compare the results obtained by all students for dissociation constant of acetic acid and find the mean value. Does the dissociation constant of a weak electrolyte depend on solution concentration?

7 Solubility Product

QUESTIONS AND PROBLEMS

1. The solubility of SnS_2 at a certain temperature is 1.1×10^{-6} mol/l. Calculate the solubility product (SP) of SnS_2.
Answer: 5.3×10^{-18}.
2. 100 ml of a saturated solution of barium sulphate at room temperature contains 2.45×10^{-4} g of $BaSO_4$. Calculate SP_{BaSO_4}.
Answer: 1.1×10^{-10}.

3. 1 ml of barium sulphate solution contains 0.001 mg Ba^{2+} ions. Is this solution saturated? $SP_{BaSO_4} = 1.1 \times 10^{-10}$.

4. 1 ml of a saturated silver carbonate solution contains 0.032 mg Ag_2CO_3. Calculate $SP_{Ag_2CO_3}$.

5. Calculate solubility of $PbCl_2$ in moles and grams per litre. $SP_{PbCl_2} = 2.4 \times \times 10^{-5}$.

Answer: 1.71 mol/l; 4.75 g/l.

6. Calculate solubility in moles and grams per litre of the following compounds:
(a) barium chromate, $SP_{BaCrO_4} = 1.6 \times 10^{-10}$;
(b) calcium carbonate, $SP_{CaCO_3} = 5 \times 10^{-9}$;
(c) lead sulphide, $SP_{PbS} = 1 \times 10^{-27}$;
(d) silver chromate, $SP_{Ag_2CrO_4} = 4 \times 10^{-12}$;
(e) manganese hydroxide, $SP_{Mn(OH)_2} = 2 \times 10^{-13}$.

Answer: (a) 1.27×10^{-5} mol/l, 3.2×10^{-3} g/l; (b) 6.9×10^{-5} mol/l; 7×10^{-3} g/l; (c) 3.17×10^{-14} mol/l; 7.57×10^{-12} g/l; (d) 1×10^{-4} mol/l; 3×10^{-2} g/l; (e) 3.68×10^{-5} mol/l; 3.27×10^{-3} g/l.

7. $SP_{ZnS} = 1.6 \times 10^{-24}$, $SP_{CdS} = 3.6 \times 10^{-9}$. The concentration of S^{2-} ion is higher in solution of which salt? How much higher?

8. What quantity, in mg, of silver is contained in 100 ml of a saturated AgCl solution and in 100 ml of a saturated Ag_2CO_3 solution? $SP_{AgCl} = 1.8 \times 10^{-10}$; $SP_{Ag_2CO_3} = 8.2 \times 10^{-12}$.

Answer: 0.14 mg and 2.5 mg.

9. How many grams of $CaCO_3$ are dissolved in 1 l of pure water and in 1 l of 0.1 *M* soda solution? $SP_{CaCO_3} = 5 \times 10^{-9}$. Assume $\alpha_{Na_2CO_3}$ to be 1.

Answer: 6.9×10^{-3} g/l; 4.8×10^{-6} g/l.

10. 0.2 g of lead sulphate precipitate was washed with 100 ml of water. What amount (in per cent) of the precipitate is lost with the washings if the washing water becomes a saturated solution of lead sulphate? $SP_{PbSO_4} = 1.6 \times 10^{-8}$.

Answer: about 2%.

11. A calcium chloride solution contains 0.1 mg of $CaCl_2$ in 1 ml. To this solution added were equal volumes of the following solutions:
1st case—0.01 *M* solution of Na_2SO_4; $SP_{CaSO_4} = 6.3 \times 10^{-5}$;
2nd case—0.01 *M* solution of Na_2CO_3; $SP_{CaCO_3} = 5 \times 10^{-9}$;
3rd case—0.01 *M* solution of $Na_2C_2O_4$; $SP_{CaC_2O_4} = 2.6 \times 10^{-9}$.
Make the appropriate calculations to decide in which case a precipitate falls out. Assume $\alpha = 1$ for all salts.

12. Decide if any substance precipitates upon mixing together equal volumes of 0.02 *M* $FeCl_2$ and 0.0002 *M* $(NH_4)_2S$ solutions. $SP_{FeS} = 5 \times 10^{-18}$. Assume $\alpha = 1$ for all salts.

13. Decide if any substance precipitates upon mixing equal volumes of 0.0001 *M* NaCl solution and a solution of $AgNO_3$ containing 0.14 mg/100 ml. $SP_{AgCl} = 1.8 \times 10^{-10}$.

14. Decide if $BaSO_4$ precipitates upon mixing equal volumes of $BaCl_2$ and Na_2SO_4 solutions each containing 0.05 g/l of solute. $SP_{BaSO_4} = 1.1 \times 10^{-10}$.

15. Decide if Ag_2CrO_4 precipitates upon mixing equal volumes of solutions containing 1.70×10^{-4} g/l of $AgNO_3$ and 1.94×10^{-5} g/l of K_2CrO_4. $SP_{Ag_2CrO_4} = 4 \times 10^{-12}$. Assume $\alpha = 1$ for all salts.

16. A dilute solution of Na_2SO_4 is added by drops to a solution containing Ba^{2+} and Ca^{2+} ions in equal concentrations. What substances and in what sequence will precipitate? Substitute ammonium oxalate $(NH_4)_2C_2O_4$ for sodium sulphate solution and answer the same question. (Consult Table 8 of Appendix).

17. Using the solubility product rule, explain dissolution of barium carbonate and zinc sulphide in hydrochloric acid. Why does zinc sulphide not dissolve in acetic acid?

18. Using the solubility product table (Table 8 of Appendix) explain why manganese(II) sulphide dissolves in hydrochloric acid, while copper sulphide does not.
19. Explain why hydrogen sulphide does not precipitate sulphides from solutions of iron(II) and manganese(II) salts, while ammonium sulphide precipitates them?
20. Explain why hydrogen sulphide does not precipitate iron sulphide from iron salt solution but precipitates CuS from a copper salt solution.

Examples of Multiple-choice Questions

When checking, use Table 8 of the Appendix. Make rough calculations.
1. The addition of which electrolytes decreases the solubility of $Mg(OH)_2$?
(1) KCl; (2) $MgSO_4$; (3) NH_4Cl; (4) NaOH; (5) Na_2SO_4.
2. Which electrolyte will precipitate Ba^{2+} ion completely?
(1) K_2CrO_4; (2) KCl; (3) $(NH_4)_2SO_4$; (4) $(NH_4)_2C_2O_4$; (5) NaOH.
3. Indicate SP of A_2B electrolyte, if its solubility is 1×10^{-4} mol/l:
(1) 3×10^{-8}; (2) 2×10^{-11}; (3) 4×10^{-12}; (4) 2×10^{-8}; (5) 3×10^{-12}.
4. Determine the amount of a substance AB (in g) contained in 100 ml of saturated solution, if $SP_{AB} = 4.9 \times 10^{-9}$; $M_{AB} = 100$.
(1) 7×10^{-7}; (2) 4.9×10^{-10}; (3) 7×10^{-4}; (4) 5×10^{-9}; (5) 9.8×10^{-9}.
5. Indicate the minimal concentration of Ba^{2+} ion (in mol/l) which is required to precipitate SO_4^{2-} ion from 0.001 *M* solution of Na_2SO_4. $SP_{BaSO_4} = 1.1 \times \times 10^{-10}$, $\alpha_{Na_2SO_4} = 1$.
1) 1.1×10^{-8}; (2) 2×10^{-8}; (3) 3×10^{-8}; (4) 1.1×10^{-7}; (5) 5×10^{-5}.

EXPERIMENT 15. SOLUBILITY PRODUCT

Apparatus and reagents

Conical test tubes.
Water. Solutions: nitric acid, 2 *N*; hydrochloric acid, 2 *N*; acetic acid, 2 *N*; sodium hydroxide, 2 *N*; sodium chloride, 0.5 *N*; sodium sulphate, 0.5 *N*; calcium chloride, 0.5 *N*; potassium iodide, 0.5 *N*; silver nitrate, 1 *N*; lead nitrate, 0.5 *N*; potassium chromate, 0.5 *N*; ammonium oxalate, 0.5 *N*; ammonium sulphide; ammonium hydroxide, 10%.

1. Precipitation

Procedure. Place 2-3 drops of iron(II) sulphate solution into two test tubes; add an equal volume of hydrogen sulphide into one and ammonium sulphide into the other test tube. In which test tube will precipitation take place?

Recording the results. Write down the ionic equation for the reaction. What is the condition for precipitation? Using the solubility product rule, explain precipitation of iron sulphide in one test tube and the absence of precipitate in the other.

2. Fractional Precipitation

Procedure. Prepare silver chloride and silver chromate in separate test tubes by acting with silver nitrate (2-4 drops) on potassium chloride and potassium chromate solutions.

Write down the ionic equations for the reactions, note the colour of the precipitates, and write down the solubility product for silver chloride and silver chromate. Which of these salts is less soluble? What substance will precipitate first from a solution containing Cl^-, CrO_4^{2-} and Ag^+ ions in equal concentrations? Prove your assumption experimentally. To that end, place 2-3 drops of potassium chloride and potassium chromate into one test tube, add 5-6 drops of water and stir the mixture by a glass rod. Carefully add 1-2 drops of silver nitrate solution and observe the reaction. What ions react first with the silver ion? What substance is formed by this reaction? Add a few drops of silver nitrate more and observe if silver chloride is formed. Note the moment when silver chloride is formed with a further increase in Ag^+ concentration.

Recording the results. Describe your observations. Write down the equations for the reactions. Explain the sequence in which the precipitates are formed in this experiment considering the solubility products of silver chloride and silver chromate. Answer the questions.

3. Completeness of Precipitation with Various Precipitants

A. Precipitation of barium salts

Procedure. Precipitate barium oxalate by acting with ammonium oxalate solution (6 drops) on barium chloride solution (4 drops). Allow the precipitate to settle and filter it on a filter paper placed in a funnel. Using a pipette, transfer 3-4 drops of a clear filtrate into two test tubes. Add 1-2 drops of ammonium oxalate solution to the first test tube to make sure that the precipitation of the barium ion is complete (with respect to the $C_2O_4^{2-}$ ion). Add 3-4 drops of potassium chromate solution to the other test tube. What substance precipitates?

Recording the results. Write down the ionic equations for the reactions. Find the solubility products of barium oxalate and barium chromate in Table 8 of Appendix, and explain precipitation of $BaCrO_4$ after removal of the Ba^{2+} ion as BaC_2O_4 from the solution. Which of the reagents precipitates the barium ion more completely?

B. Precipitation of lead salts

Procedure. Prepare lead chloride by the reaction between lead nitrate (4 drops) and sodium chloride (6 drops). Filter the solution into two test tubes (2-3 drops into each test tube). Add equal volumes (2-3 drops) of potassium iodide solution into one test tube and of sodium chloride into the other. Which salt precipitates?

Recording the results. Write down the ionic equations for the reactions by which lead salts are produced. Using your observations, compare the solubility products of these salts. Consult Table 8 to see if your conclusion is correct.

4. Conditions for Dissolution of Precipitates

A. Dependence of solubility on solubility product

Procedure. Precipitate chloride, bromide and iodide of silver in three separate test tubes by acting with silver nitrate on the corresponding salts (2-3 drops of each reagent).

Note the colour of the precipitates. Add 2-3 drops of ammonium hydroxide to each test tube and stir the mixtures using a glass rod. In which test tube the dissolution process occurs quickly? What precipitate does not practically dissolve?

Recording the results. Write down the equations for dissolution of silver halides in an aqueous ammonia solution with formation of the complex ion $[Ag(NH_3)_2]^+$. Write down expressions of the solubility products for chloride, bromide and iodide of silver and indicate their numerical values. Explain dissolution of the silver halides in ammonium hydroxide. Why does silver bromide dissolve in ammonium hydroxide slower than silver chloride, whereas silver iodide is practically insoluble in this reagent?

B. Dependence of solubility on concentration of solvent ions

Procedure. Precipitate calcium oxalate in two test tubes by the reaction between a calcium salt solution and ammonium oxalate (2-3 drops). Add a 2 *N* hydrochloric acid to one test tube by drops until complete dissolution of the precipitate. Add the same amount of a 2 *N* acetic acid to the other test tube. Observe insolubility of calcium oxalate in the second test tube.

Recording the results. Write down the ionic equations for the reactions and the expression for the solubility product. Explain why calcium oxalate is soluble in hydrochloric acid and practically insoluble in acetic acid. The concentration of which ion influences the solubility of calcium oxalate in acids?

5. Reprecipitation of Sparingly Soluble Substances

A. Preparing lead sulphide from lead sulphate

Procedure. Place 2 drops of lead nitrate into a test tube and add 3 drops of sodium sulphate solution. What substance precipitates? Write down the ionic equation for the reaction.

Allow the precipitate to settle and remove the liquid phase using a piece of filter paper. Add 3-4 drops of ammonium sulphide to the precipitate and stir the mixture using a glass rod. How does the colour change? What substance has formed?

Recording the results. Describe your observations. Answer the questions. Write down the expressions for the solubility products and their numerical values (see Table 8, Appendix) for the obtained sparingly soluble substances. Explain the conversion of one substance into another.

B. Preparing lead chromate from lead sulphate

Procedure. Carry out the experiment as instructed in 5*A*. Prepare lead sulphate and convert it into lead chromate. How does the colour of the precipitate change?

Recording the results. Write down the equations for the reactions. Write down the values for the solubility products of the prepared sparingly soluble substances and explain the conversion of lead sulphate into lead chromate.

8 Hydrogen Ion Concentration (pH). Buffer Solutions. Hydrolysis of Salts

QUESTIONS AND PROBLEMS*

1. How does the ionic equilibrium of water and its degree of dissociation change if a strong acid or strong base is added? How will the concentration of H^+ and OH^- ions change? Can the concentration of H^+ and OH^- ions be equal to zero in an aqueous solution? Explain your answer.
2. Determine the pH of the following solutions assuming that HCl and NaOH fully dissociate: (a) 0.1 *N* HCl; (b) 0.05 *N* HCl; (c) 0.01 *N* NaOH; (d) 0.2 *N* NaOH; (e) 0.1 *N* HCN (assume the dissociation degree to be 0.01%); (f) 0.1 *N* ammonium hydroxide $NH_3 \cdot H_2O$ (assume the dissociation degree to be 1%). Answer: (a) 1; (b) 1.3; (c) 12; (d) 13.3; (e) 5; (f) 11.
3. Determine the pH of the following solutions using the dissociation constants of the corresponding acids and bases (see Table 7 of Appendix): (a) 0.1 *N*

* Aqueous solutions are understood in all questions and problems.

CH_3COOH; (b) 0.05 *N* HCN; (c) 0.001 *N* HClO; (d) 0.2 *N* $NH_3 \cdot H_2O$; (e) 0.01 *N* $NH_3 \cdot H_2O$.
Answer: (a) 3.87; (b) 5.83; (c) 5.25; (d) 11; (e) 10.62.
4. The pH of a solution is 2 and of another solution 6. One litre of which solution has a higher concentration of the H^+ ions? How much higher?
5. Determine the concentration of H^+ ions and the pH of solutions if OH^- ion concentration in them is (in mol/l): (a) 10^{-8}; (b) 10^{-1}; (c) 10^{-2}; (d) 4×10^{-3}.
6. Specify the medium (acidic, neutral, or alkaline) and determine the concentration of H^+ and OH^- ions (in mol/l) in solutions whose pH is: (a) 3; (b) 9; (c) 7; (d) 1.6; (e) 10.5.
7. Calculate the molar concentration of a monobasic acid HA in a solution if (a) pH = 4, $\alpha = 0.01$; (b) pH = 3, $\alpha = 1\%$; (c) pH = 5.8, $\alpha = 0.001$.
Answer: (a) 0.01 *M*; (b) 0.1 *M*; (c) 0.06 *M*.
8. Calculate the degree and dissociation constant of the base MeOH in a solution if (a) pH = 8, $c = 0.001$ mol/l; (b) pH = 10, $c = 0.01$ mol/l; (c) pH = = 11.6, $c = 0.2$ mol/l.
Answer: (a) $\alpha = 0.1\%$; $K = 10^{-9}$; (b) $\alpha = 1\%$, $K = 10^{-6}$; (c) $\alpha = 2\%$, $K = = 8 \times 10^{-5}$.
9*. Determine the pH of a solution of the acid H_2A if (a) $c = 1$ mol/l, $\alpha = 3\%$; (b) $c = 0.1$ mol/l, $\alpha = 5\%$; (c) $c = 0.05$ mol/l, $\alpha = 1\%$.
Answer: (a) 1.22; (b) 2; (c) 3.
10*. Calculate the pH of a 0.05 *M* solution of $Me(OH)_2$ if $\alpha = 10\%$.
Answer: pH = 12.
11. Calculate the pH of buffer mixtures prepared by mixing together equal volumes of (a) 0.1 *M* CH_3COOH and 0.1 *M* $NaCH_3COO$; (b) 0.1 *M* CH_3COOH and 0.01 *M* $NaCH_3COO$; (c) 0.001 *M* CH_3COOH and 0.1 *M* $NaCH_3COO$.
Answer: (a) 4.76; (b) 3.76; (c) 6.76.
12. Calculate the pH of the following buffer mixtures prepared by pouring together equal volumes of the following solutions: (a) 0.1 *M* $NH_3 \cdot H_2O$ and 0.1 *M* NH_4Cl; (b) 0.2 *M* $NH_3 \cdot H_2O$ and 0.02 *M* NH_4Cl; (c) 0.2 *M* $NH_3 \cdot H_2O$ and 0.2 *M* NH_4Cl.
Answer: (a) 9.25; (b) 10.25; (c) 9.25.
13. How will the pH of a formate buffer (HCOOH + HCOONa) change if (a) the concentration of the salt is increased 100 times; (b) the concentration of the salt is decreased 10 times?
Answer: (a) increases by 2; (b) decreases by 1.
14. How will the pH of an ammonia buffer ($NH_3 \cdot H_2O + NH_4Cl$) change if (a) the concentration of NH_4Cl is increased 10 times; (b) the concentration of $NH_3 \cdot H_2O$ is decreased 10 times?
Answer: the pH decreases by 1 in both cases.
15. What is the reaction of aqueous solutions of ammonium nitrate, potassium nitrate, potassium cyanide, ammonium cyanide and ammonium acetate? Explain your answer and write down the corresponding reaction equations.
16. Indicate which of the following salts will hydrolyze and what form of hydrolysis (simple, stepped, complete) will take place in each case:
(a) NaClO; (b) NaCl; (c) K_3PO_4; (d) Al_2S_3; (e) $Fe(NO_3)_3$.
17. Will hydrolysis of sodium cyanide be accelerated or slowed down if the following solutions are added to the salt: (a) acid; (b) alkali; (c) ammonium chloride?
18. Explain the different hydrolysis of the following salts (using Tables 6 and 10 of Appendix):
(a) NaCN; (b) $NaCH_3COO$; (c) NH_4CH_3COO.
19. Write down the ionic equations for the first step of hydrolysis of potassium carbonate, sodium phosphate, and ammonium sulphate. In which case will the hydrolysis degree be the highest and in which the lowest? Explain your answer.

* Assume α to be summary for two steps of dissociation.

20. Write down the ionic and molecular equations for all steps of hydrolysis of the following salts: (a) sodium sulphide; (b) aluminium acetate; (c) iron(II) sulphate. How can the hydrolysis of each salt be accelerated or slowed down? Why does the degree of hydrolysis decrease at each next step?
21. Calculate the constant and degree of hydrolysis h and pH at room temperature in solutions of salts hydrolyzing with respect to the anion of a weak monobasic acid: (a) 0.1 M $NaCH_3COO$; (b) 0.1 M KCN; (c) 0.01 M KCN.
Answer: (a) $K_{hydr} = 5.7 \times 10^{-10}$, $h = 7.6 \times 10^{-5}$ or 0.0076%, pH = 8.88; (b) $K_{hydr} = 1.6 \times 10^{-5}$, $h = 0.013$ or 1.3%, pH = 11.1; (c) $K_{hydr} = 1.6 \times \times 10^{-5}$, $h = 0.04$ or 4%, pH = 10.6.
22. Calculate K_{hydr}, the degree of hydrolysis h, and pH at room temperature in solutions of salts hydrolyzing with respect to the cation of a monohydric base: (a) 0.1 M ammonium chloride, (b) 0.01 M ammonium chloride and (c) 0.1 M ammonium nitrate.
Answer: (a) $K_{hydr} = 5.6 \times 10^{-10}$, $h = 7.4 \times 10^{-5}$ or 0.0074%, pH = 5.12; (b) $K_{hydr} = 5.6 \times 10^{-10}$, $h = 2.38 \times 10^{-4}$ or 0.0238%, pH = 5.62; (c) $K_{hydr} = 5.6 \times 10^{-10}$, $h = 7.4 \times 10^{-5}$ or 0.0074%, pH = 5.12.
23. Calculate K_{hydr}, the degree of hydrolysis h, and pH at room temperature in solutions of salts formed by a monobasic weak acid and a monohydric weak base: (a) 0.1 M NH_4CH_3COO solution, (b) 0.1 M NH_4CN solution.
Answer: (a) $K_{hydr} = 3.2 \times 10^{-5}$, $h = 5.7 \times 10^{-3}$ or 0.57%, pH = 7; (b) $K_{hydr} = 0.912$, $h = 0.488$ or 48.8%, pH = 9.22.
24. Calculate K_{hydr}, the degree of hydrolysis h, and pH at room temperature of solutions of salts formed by weak polybasic acids and weak polyhydric bases, assuming that hydrolysis occurs only at the first step: (a) 0.1 M $Cd(NO_3)_2$; (b) 1 M $AlCl_3$; (c) 0.01 M Na_2CO_3.
Answer: (a) $K_{hydr} = 2 \times 10^{-12}$, $h = 4.6 \times 10^{-6}$ or 0.0005%, pH = 6.45; (b) $K_{hydr} = 7.1 \times 10^{-4}$, $h = 2.8 \times 10^{-2}$ or 2.8%, pH = 1.57; (c) $K_{hydr} = = 1.8 \times 10^{-4}$, $h = 1.3 \times 10^{-1}$ or 13%, pH = 11.2.
25. Calculate the molar concentration, constant and degree of hydrolysis of salts in the following solutions from their pH: (a) NH_4Cl, pH = 5.62; (b) NH_4NO_3, pH = 6.12; (c) $NaCH_3COO$, pH = 8.36; (d) KCN, pH = 11.57.
Answer: (a) $c = 0.01$ mol/l, $K_{hydr} = 5.6 \times 10^{-10}$, $h = 2.38 \times 10^{-4}$ or 0.024%; (b) $c = 0.001$ mol/l, $K_{hydr} = 5.6 \times 10^{-10}$, $h = 7.5 \times 10^{-4}$ or 0.075%; (c) $c = = 0.01$ mol/l, $K_{hydr} = 5.7 \times 10^{-10}$, $h = 2.8 \times 10^{-4}$ or 0.028%; (d) $c = 1$ mol/l, $K_{hydr} = 1.4 \times 10^{-5}$, $h = 3.75 \times 10^{-3}$ or 0.375%.

Examples of Multiple-choice Questions

1. The concentration of OH^- ions in an aqueous solution is 10^{-2} mol/l. What is the pH of the solution?
(1) 5; (2) 6; (3) 11; (4) 12; (5) 13.
2. What is the degree of dissociation of acetic acid in a 0.01 N solution if its pH is 5?
(1) 10%; (2) 1%; (3) 0.1%; (4) 0.01%; (5) 0.001%.
3. The pH of which solution is higher than 7?
(1) $Ca(CN)_2$; (2) $Zn(NO_3)_2$; (3) NH_4Cl; (4) KCl; (5) Na_2CO_3.
4. Which salts hydrolyze to form basic salts?
(1) Na_3PO_4; (2) K_2CO_3; (3) $ZnCl_2$; (4) $Al_2(SO_4)_3$; (5) $(NH_4)_2SO_4$.
5. How can the degree of hydrolysis of Na_2S be decreased?
(1) by raising temperature; (2) by lowering temperature; (3) by adding KOH; (4) by adding HCl; (5) by diluting the solution.

EXPERIMENT 16. INDICATORS. DETERMINING pH OF SOLUTIONS. BUFFER SOLUTIONS

Apparatus and reagents

pH-Meter.
Beakers, 20-30-ml. Glass rods.
Pipettes.
Indicators: litmus, phenolphthalein, methyl orange, methyl red, thymol blue, alizarin yellow, indigo carmine, universal indicator paper.
Solutions: hydrochloric acid, 0.1 *N*; acetic acid, 0.1 *N*; sodium hydroxide, 0.1 *N* and 1 *N*; ammonium hydroxide, 0.1 *N*; sodium acetate, 0.1 *N*; ammonium chloride, 0.1 *N*.

1. Determining pH Using Indicators

A. Colour of some indicators in various media

Acid-base indicators are used to determine pH of medium. These are mostly weak organic acids or bases, whose undissociated molecules or ions account for the solution colour. For example, undissociated molecules of phenolphthalein are colourless, while its anions colour the solution red. If we indicate the phenolphthalein molecule, which is a weak acid, as HInd, its dissociation in aqueous solution can be expressed as follows:

$$\underset{\text{colourless}}{\text{HInd}} \rightleftarrows \text{H}^+ + \underset{\text{red}}{\text{Ind}^-}$$

If a strong acid is added to this solution, or vice versa, phenolphthalein is added to an acid, the dissociation equilibrium will be shifted to the left; H^+ ions of the strong acid will almost completely bind the coloured Ind^- ions into a colourless molecule of the indicator (HInd) and the solution becomes colourless. If an alkali is added to the phenolphthalein solution (or phenolphthalein is added to an alkali solution), OH^- ions will bind H^+ ions of phenolphthalein and the dissociation equilibrium will be shifted to the right, in the direction of increasing the number of Ind^- ions: the solution turns red.

Each indicator changes its colour within a certain pH range (specific for this indicator), which is called the pH range of indicator. For example, a solution is colourless in the presence of phenolphthalein at $pH \leqslant 8$, while it turns intense red at $pH \geqslant 10$. The pH range of phenolphthalein is thus from 8 to 10 (the alkaline medium). The pH range of an indicator may be in the acidic or alkaline medium, but the indicator form, in which it exists in solution with pH below the lower limit of its pH range, is called acidic form of an indicator, while the form in which it exists at pH above the upper limit of its pH range, is called alkaline form of an indicator. At values falling within the pH range of an indicator, the solution colour

is mixed, with hues of both acidic or alkaline form; the prevalence of colour depends on a particular pH of the medium.

Procedure. Identify the colour of acidic and alkaline forms of most common four indicators: methyl orange, methyl red, litmus, and phenolphthalein. Observe their colour in strong acidic and strong alkaline media, when the pH is definitely below or above the pH range of the indicator. To do so, place 10 drops of a 0.1 *N* hydrochloric acid into four labelled test tubes, and the same amount of a 0.1 *N* sodium hydroxide solution into another four test tubes labelled by the same numerals. Put the test tubes in the rack. Arrange them so that test tube No. 1 containing acid stands next to test tube No. 1 containing alkali, and so on. Now add a drop of methyl orange indicator into the test tubes labelled No. 1, a drop of methyl red to test tubes No. 2, 5 drops of litmus to test tubes No. 3 (a smaller amount of litmus will not be obvious), and a drop of phenolphthalein to test tubes No. 4.

Recording the results. Write down your observations in the table as indicated below:

Indicator	pH range	Indicator colour		
		acidic form	transition range	alkaline form
Methyl orange	3.1-4.4		Orange	
Methyl red	4.4-6.2		Orange	
Litmus	5.0-8.0		Violet	
Phenolphthalein	8.2-10.0		Pink	

Which indicator has its pH range close to the neutral medium? The pH range of which indicator falls within the acid pH values? alkaline pH values? Determine the pH of a 0.1 *N* hydrochloric acid solution and decide if one can observe the colour of the acidic form of thymol blue in this solution? (Consult Table 9.) Determine the pH of a 0.1 *N* sodium hydroxide solution and decide the alkaline form of which indicator (from the list of indicators given in Table 9 of Appendix) is invisible in this solution.

B. Determining pH of solution using indicator sets

The pH of a solution can be determined by observing the colour change after adding various indicator solutions. Each indicator is added to a separate portion of the test solution. The pH value of a medium is determined as an arithmetic mean of extreme values of pH range of indicators after several observations. A set of indicators can be used to determine pH of a medium to an accuracy of $\pm$ 0.5 pH. The

test should begin with an indicator whose pH range is the nearest to pH = 7.

Procedure. Obtain 3-4 ml of test solution from the instructor. Place a solution of neutral litmus into a test tube to 1/3 its capacity. Add 3-4 drops of the test solution and stir using a glass rod. Note the colour of the solution. If the solution turns red, the reaction of the test solution is acidic, i.e. pH $\leqslant$ 5. If the solution turns blue, it reacts alkaline, i.e. its pH $\geqslant$ 8. If the colour does not change, the test solution is neutral, i.e. its pH is about 7.

If the solution reaction is acidic to litmus, check the pH by consulting Table 9 of Appendix. To do so, act as follows. Place 5 drops of the test solution into another test tube and add a drop of methyl red. If the solution turns orange, its pH can be considered to be about 5 (within the pH range of the indicator). Red colour of the solution indicates that pH $\leqslant$ 4.4. The determination of the pH should then be continued. Take another clean test tube, place 5 drops of the test solution into it and add a drop of methyl orange. If the solution turns orange yellow, the pH $\geqslant$ 4.4. Summarizing the observations with methyl red and methyl orange, one can conclude that pH is 4.4. If the solution turns red from methyl orange, the pH $\leqslant$ $\leqslant$ 3.1. In this case, take another clean test tube, place 5 drops of the solution, and add a drop of thymol blue. If the solution turns yellow (the first pH range), the pH of the solution is $>$2.8. Consider the result of the test with methyl orange and thymol blue and conclude that 2.8 $<$ pH $<$ 3.1. Assume the pH to be (3.1 + 2.8)/2 = 2.95.

If the solution reacts alkaline to litmus, determine its pH as described above using the indicators whose pH range falls within the alkaline pH values, beginning with phenolphthalein or thymol blue (the second pH range).

Describe the procedure in the log-book and write down the experimentally found pH value of the test solution. Determine the hydrogen ion concentration from the pH value. Consult the instructor to check the result of your determination of pH and the hydrogen ion concentration of the test solution.

C. Determining pH of solution using universal indicator

The so-called universal indicators are very convenient for tentative determination of pH of a solution. These indicators are mixtures of several indicators that change the colour within a broad range of pH values. The universal indicator is used to impregnate strips of paper which are then dried and supplemented with a standard colour scale by which the pH of a test solution can be identified by colour matching. Universal indicators are used as solutions too. To that end, a series of standards is prepared in sealed vessels with indication of pH corresponding to the colour of standard solution.

Procedure. Obtain a test solution with unknown pH from the instructor. Using a pipette, transfer 2-3 drops of the solution onto an indicator paper. Determine the pH of the test solution by matching colours of the wet spot on the paper with the standard colour scale. Colours of the standard scale correspond only to whole numbers of pH; if the colour of the test solution is intermediate of two neighbouring colours of the scale, fractions of pH can be determined approximately. Draw your conclusion on the pH and the reaction of the test solution. Consult the instructor to check your conclusion.

2. Buffer Solutions

Solutions capable of preserving their pH practically unaltered during their dilution or mixing with definite amounts of strong acids or alkalies are often used in laboratory and industrial processes. These solutions are called buffers*.

Common buffer solutions are mixtures of a weak acid and a salt formed by this acid and a strong base, e.g. (CH_3COOH + + $NaCH_3COO$)—an acetate buffer, (C_6H_5COOH + NaC_6H_5COO)—benzoate buffer. Or a buffer can be a mixture of a weak base and a salt formed by this base and a strong acid, e.g. an ammonium buffer: $NH_3 \cdot H_2O$ + NH_4Cl. Buffer solutions of weak acids have the $pH < 7$, and of weak bases $pH > 7$.

Buffer mixtures maintain pH practically unaltered because their components bind H^+ ions of acids or OH^- ions of bases that are added to the solution or are formed in the solution by some reactions. For example, if a strong acid is added to an acetate buffer, H^+ ions of the acid combine with CH_3COO^- ions of the salt into low-dissociating molecules CH_3COOH, rather than increase the hydrogen ion concentration in solution. When alkali is added, OH^- ions bind H^+ ions of the buffer into low-dissociating molecules of water, while the hydrogen ion concentration is restored immediately because the equilibrium $CH_3COOH \rightleftarrows H^+ + CH_3COO^-$ shifts in the direction of increasing dissociation of acetic acid. The pH of the medium thus remains practically unaltered in both cases. The mechanism of action of the ammonium buffer solution is similar.

Solutions of some salts or their mixtures, e.g. $NaHCO_3$ + Na_2CO_3, $Na_2B_4O_7$, also have buffering properties.

A. Preparing buffer solutions

Procedure. Prepare an acetate buffer (CH_3COOH + $NaCH_3COO$). To do so, place 5 ml of a 0.1 *M* acetic acid solution and the same amount

* The buffer capacity is determined by the maximum amount of strong acid or alkali that can be added to it without altering the pH. This aspect will not be discussed in this text-book.

of sodium acetate into a small beaker and stir the mixture using a glass rod.

Take another beaker to prepare an ammonium buffer ($NH_3 \cdot H_2O$ + + NH_4Cl) from 0.1 *M* solutions of ammonia and ammonium chloride.

Determine the pH of thus prepared solutions using a universal indicator (see part 1*C* of the experiment). Save the solutions for parts 2*B*, *C* and *D*.

Recording the results. Describe the procedure for preparing buffer mixtures and write down their pH values found experimentally. Calculate the pH of the acetate buffer following these considerations: the salt $NaCH_3COO$ is a strong electrolyte and can be assumed to dissociate completely into ions. The high concentration of CH_3COO^- ion practically inhibits dissociation of the weak acetic acid. The equilibrium concentration of undissociated molecules of acetic acid can therefore be considered equal to its starting molar concentration: $[CH_3COOH]_{equil} = c_{acid}$, while the concentration of CH_3COO^- ion in solution, to molar concentration of the salt: $[CH_3COO^-]_{sln} = c_{salt}$. The dissociation constant for acetic acid in the buffer is then

$$K_{acid} = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]} = \frac{[H^+]\, c_{salt}}{c_{acid}}$$

whence

$$[H^+] = K_{acid} \frac{c_{acid}}{c_{salt}}$$

Find the logarithm for the expression and reverse the signs to obtain a formula by which the pH of buffer solutions of weak acids and their salts can be determined:

$$pH = pK_{acid} - \log \frac{c_{acid}}{c_{salt}}$$

where $pK_{acid} = -\log K_{acid}$.

In our case $c_{acid} = c_{salt}$; therefore $\log (c_{acid}/c_{salt}) = 0$ and the pH is therefore $-\log K_{acid}$. (For the value of K_{CH_3COOH}, see Table 7 of Appendix.)

Use the derived formula to calculate the pH of the acetate buffer and compare the result with the experimentally determined value.

Following similar considerations one can show that pH of the ammonium buffer can be determined by the formula

$$pH = 14 - pK_{base} + \log \frac{c_{base}}{c_{salt}}$$

where $pK_{base} = -\log K_{base}$.

Use this formula to calculate the pH of the prepared buffer solution and compare the result with the value determined with the use of

the universal indicator. (For the value of $K_{NH_3 \cdot H_2O}$, see Table 7 of the Appendix.)

B. Examining properties of acetate buffer solution

Procedure. Use the universal indicator to determine the pH of distilled water. Place 10 drops of distilled water into two test tubes and add a drop of a 0.1 *N* hydrochloric acid to one, and a drop of a 0.1 *N* NaOH solution to the other test tube. Stir the solutions using glass rods, and determine the pH of the obtained solutions.

Place 10 drops of the acetate buffer (prepared in part 2*A* of the experiment) into two other test tubes. If the pH of the buffer is still unknown, determine it. Add a drop of a 0.1 *N* hydrochloric acid to one, and a drop of a 0.1 *N* NaOH solution to the other test tube. Stir the solutions using glass rods. Determine the pH of the solutions again.

Recording the results. Write down the found data into the following table:

Initial solution	Found pH value		
	in initial solution	after adding HCl	after adding NaOH
Distilled water			
Acetate buffer ($CH_3COOH + NaCH_3COO$)			

How does the pH of distilled water change after addition of HCl or NaOH? How does the pH of the buffer solution change after addition of the same reagents?

C. Examining properties of ammonium buffer

Procedure. Place 10 drops of the ammonium buffer prepared in part 2*A* of the experiment (if its pH is unknown determine it) into two test tubes. Add a drop of a 0.1 *N* HCl into one and a drop of a 0.1 *N* NaOH solution into the other test tube. Determine the pH of thus obtained mixtures using the universal indicator. Compare the obtained pH value with the pH of the buffer.

Repeat the experiment with distilled water: measure the pH of distilled water, then add a drop of a 0.1 *N* HCl solution to ten drops of distilled water and a drop of a 0.1 *N* NaOH solution to another ten-

drop portion of distilled water. Measure the pH of thus prepared solutions and conclude on the effect of the addition of HCl and NaOH to distilled water and the buffer solution.

D. Effect of dilution on pH of buffer solutions

Procedure. Place 1 ml of the acetate buffer prepared in part 2*A* of the experiment (if its pH is unknown, determine it) into a 100-ml volumetric flask and add about 50 ml of water. Shake the flask to stir the solution and then determine its pH using a universal indicator. Add water to the mark (i.e. dilute 100 times), close the flask with a stopper, shake the solution and again determine its pH. Does the pH of the buffer change as it is diluted 50 and then 100 times? Carry out a similar procedure using ammonium buffer solution instead of the acetate buffer.

3. Determining pH by Means of a pH-meter

If the accuracy of pH determination should be not worse than ± 0.02 pH, an apparatus known as a pH-meter is used. Its design may vary, and it is therefore necessary to study the operating instructions for a particular pH-meter available in the laboratory. Obtain a test solution from the instructor and determine its pH.*

Consult the instructor to check your result.

EXPERIMENT 17. HYDROLYSIS OF SALTS

Apparatus and reagents	Solutions:
Water bath. Sodium acetate. Sodium carbonate. Ammonium carbonate. Potassium chloride. Aluminium chloride. Tin(II) chloride. Sodium sulphite. Ammonium acetate. Universal indicator paper. Litmus (neutral). Phenolphthalein.	sodium acetate, 0.5 *N*; sodium carbonate, 0.5 *N*; aluminium chloride, 0.5 *N*; magnesium chloride, 0.5 *N*; antimony(III) chloride, 0.5 *N*; ammonium sulphide, 0.5 *N*; tin(II) chloride, 0.5 *N*; ammonium chloride, 0.1 *N*; hydrochloric acid, 2 *N*.

1. pH of Salt Solutions

Procedure. Fill seven test tubes to 1/3 their capacity with a neutral litmus solution. Save one test tube as a reference and add a microspatula of crystals of sodium acetate, aluminium chloride, sodium carbonate, ammonium carbonate, potassium chloride, and ammonium

* The pH-meter should be adjusted by the laboratory assistant.

acetate into the other six test tubes, respectively. Stir the solutions by separate glass rods. (Never use the same rod to stir different solutions.)

Conclude on the pH of the solutions by the change of litmus colour.

Recording the results. Tabulate the results as follows:

Test tube No.	Salt formula	Litmus colour	Reaction of medium	pH of solution ($pH < 7$, $pH = 7$, $pH > 7$)

Which of the salts are hydrolyzed? Write down the net ionic and molecular equations for the reactions of hydrolysis and specify the type of hydrolysis for each salt (simple or stepped).

If the hydrolysis is stepped, write down the equations only for the first step since the next steps are very slow in sufficiently concentrated solutions. Make general conclusions concerning the pH of solutions of salts of

(a) strong bases and weak acids;
(b) weak bases and strong acids;
(c) weak bases and weak acids;
(d) strong bases and strong acids.

2. Formation of Basic and Acidic Salts During Hydrolysis

A. Hydrolysis of aluminium acetate

Procedure. Place 7-8 drops of aluminium chloride solution in a test tube and add an equal volume of sodium acetate solution. Fix the test tube in a clamp of a stand and lower into a boiling water bath. Observe precipitation of a basic salt of aluminium $Al(OH)_2CH_3COO$.

Recording the results. Write down the molecular equation for the formation of aluminium acetate and the ionic equation for its hydrolysis. At which hydrolysis step does a basic salt precipitate? Which salts hydrolize to give basic salts?

B. Hydrolysis of sodium sulphite

Procedure. Fill a test tube 1/3 full with water. Add 1-2 microspatulas of sodium sulphite crystals and stir by a glass rod. Place two drops of the prepared solution on an indicator paper and determine its pH.

Which ions in the solution account for this pH? By what process are they formed?

Make sure that the sodium sulphite has partly hydrolyzed (the absence of the odour of sulphur dioxide). What salt forms at the first hydrolysis step?

Write down the molecular and net ionic equations for the hydrolysis of sodium sulphite. Which salts hydrolize to give acidic salts?

3. Complete (Irreversible) Hydrolysis of Salts

Procedure. Place 6-8 drops of aluminium chloride solution into each of two test tubes. Add the same volume of ammonium sulphide solution to one, and of sodium carbonate to the other test tube. Note evolution of hydrogen sulphide in the first test tube (by the smell) and observe bubbling in the second test tube (liberation of carbon dioxide). Aluminium hydroxide precipitates in both test tubes.

Recording the results. Write down the equations for the reactions by which aluminium hydroxide is formed. Why is aluminium carbonate or aluminium sulphide not formed?

4. Factors Affecting Hydrolysis of Salts

A. Effect of strength of a salt-forming acid and base on the degree of salt hydrolysis

Procedure. Fill two test tubes 2/3 full with distilled water and add a microspatula of sodium sulphite crystals into one test tube and the same quantity of crystalline sodium carbonate into the other. Add a drop of phenolphthalein solution to both.

Write down the ionic equations for hydrolysis of sodium sulphite and sodium carbonate (the first step). In which solution is the colour of phenolphthalein more intense? In which solution is the concentration of OH^- ions higher? Which salt is hydrolyzed stronger? Why?

The degree of hydrolysis of which salt is higher: $AlCl_3$ or $MgCl_2$, provided their concentrations and the temperature are the same? In which of these solutions is the hydrogen ion concentration higher? Prove your answer experimentally by determining tentatively (by indicator paper) the pH of these salt solutions.

Derive a general conclusion on the effect of strength of salt-forming acid and base on the degree of salt hydrolysis.

B. Effect of temperature on the degree of salt hydrolysis

Procedure. Half fill a test tube with distilled water and add 2-3 microspatulas of sodium acetate.

Write down the ionic equation for hydrolysis of this salt. Is the pH of the sodium acetate solution below or above 7?

Add a drop of phenolphthalein to the salt solution in the test tube and place it in a boiling water bath.

Recording the results. What conclusion on the change of OH^- ion concentration in solution can be drawn from the change of phenolphthalein colour during heating? In what direction does the hydrolysis equilibrium shift? Cool the test tube in cold water. Does the hydrolysis equilibrium shift again after cooling?

Formulate the effect of temperature on the degree of salt hydrolysis. Indicate the causes of this effect.

C. Effect of dilution on the degree of salt hydrolysis

Procedure. Place 2-3 drops of antimony(III) chloride solution in a test tube and add water by drops to precipitate white antimony oxichloride SbOCl. This precipitate forms at the second step of hydrolysis from $Sb(OH)_2Cl$ due to splitting off a water molecule.

Recording the results. Write down the net ionic equations for the first and the second steps of hydrolysis of antimony(III) chloride and the overall equation for its hydrolysis to $Sb(OH)_2Cl$. Write down the expression for the hydrolysis constant of antimony(III) chloride (the first step). Use this constant to illustrate the effect of dilution on the degree of salt hydrolysis. What reagent can lower the degree of hydrolysis of antimony(III) chloride? Prove your answer experimentally.

Draw a general conclusion concerning the effect of dilution on the degree of salt hydrolysis. The degree of hydrolysis of which salts does not change with dilution?

D. Effect of hydrogen ion concentration on salt hydrolysis

Procedure. Place 8-10 drops of distilled water and a microspatula of tin(II) chloride crystals into a test tube and stir the solution with a glass rod: white basic tin salt SnOHCl is precipitated. By what process is the salt formed?

Write down the ionic equation for the reaction. Which ion concentration should be increased in order to suppress the hydrolysis? Add this ion. Has the precipitate dissolved?

5. Determining Constant and Degree of Salt Hydrolysis from pH of Solution*

Procedure. Determine the constant and degree of hydrolysis of ammonium chloride in 0.1 *M* and 0.001 *M* solutions and decide if

* The method is applicable to salts with small degree of hydrolysis ($h < < 10\%$).

they depend on concentration. (Any other hydrolyzing salt can be used instead of ammonium chloride.)

Obtain a 0.1 *M* solution of NH_4Cl from the laboratory assistant and determine its pH by a suitable method (described in Experiment 16). Prepare a 0.001 *M* NH_4Cl solution. To that end, rinse a 10-ml pipette with a 0.1 *M* solution obtained from the laboratory assistant, measure 10 ml of the solution and transfer it into a 1-litre flask. Add water to the mark, stopper the flask and stir thoroughly by turning the flask up and down several times. If a volumetric flask of 1-litre capacity is not available, a 0.001 *M* solution can be prepared by two-fold dilution: the 10-ml portion of a 0.1 *M* solution is first diluted 10 times in a 100-ml flask. Rinse the pipette with this diluted solution and transfer a 10-ml portion into another 100-ml flask where it is again diluted with water to the mark. Determine the pH of the 0.001 *M* ammonium chloride solution by the same method (as was used for the first determination).

Recording the results. Write down the pH values found experimentally for 0.1 *M* and 0.001 *M* ammonium chloride solutions.

Calculate the hydrolysis constants for the salt K_{hydr} from the experimentally found pH values bearing in mind the following: in accordance with the equation of hydrolysis of NH_4Cl

$$NH_4^+ + H_2O \rightleftarrows NH_3 \cdot H_2O + H^+$$

the hydrolysis constant is

$$K_{hydr} = \frac{[NH_3 \cdot H_2O][H^+]}{[NH_4^+]}$$

It can be seen from the equation that $[NH_3 \cdot H_2O] = [H^+]$. Since the dissociation of salt with low degree of hydrolysis is practically complete, the equilibrium concentration of the NH_4^+ ion differs but little from the initial one, i.e. it can be assumed that $[NH_4^+]_{eq} = c_{salt}$. The formula for calculations can thus be derived:

$$K_{hydr} = \frac{[H^+]^2}{c_{salt}}$$

The concentration of salt in solution (c_{salt}) is known: 0.1 *M*, and 0.001 *M*, while the concentration of the H^+ ion can be determined for each particular case from experimentally found pH.

The degree of hydrolysis *h* is related to the hydrolysis constant as follows:

$$K_{hydr} = c_{salt} h^2$$

whence

$$h = \sqrt{K_{hydr}/c_{salt}}$$

Calculate the degree of NH_4Cl hydrolysis for both solutions in question.

Compare the experimentally found values for K_{hydr} and h in 0.1 M and 0.001 M solutions of NH_4Cl with the calculated values. Derive your conclusion concerning the effect of salt concentration (dilution) on the constant and degree of salt hydrolysis at constant temperature. Will K_{hydr} change with increasing temperature? Explain your answer.

9 Oxidation-reduction Reactions

QUESTIONS AND PROBLEMS

1. Which of the following are oxidation-reduction reactions?
(a) $Zn + H_2SO_4$ (dilute) $= ZnSO_4 + H_2$
(b) $Zn + 2H_2SO_4$ (conc.) $= ZnSO_4 + SO_2 + 2H_2O$
(c) $Zn(OH)_2 + H_2SO_4 = ZnSO_4 + 2H_2O$
(d) $Fe_2O_3 + CO = CO_2 + 2FeO$
(e) $Fe_2O_3 + 6HCl = 2FeCl_3 + 3H_2O$
(f) $Na_2CO_3 + SiO_2 = Na_2SiO_3 + CO_2$
(g) $2Na_2SO_4 + 2SiO_2 + C = 2Na_2SiO_3 + CO_2 + 2SO_2$

Reason your answers and indicate the oxidant and the reductant in each reaction.
2. Decide if oxidation or reduction occurs in the following conversions:
(a) $FeSO_4 \rightarrow Fe_2(SO_4)_3$; (b) $Fe_2O_3 \rightarrow Fe$; (c) $NH_3 \rightarrow NO$; (d) $Cl^- \rightarrow ClO_4^-$; (e) $2Cl^- \rightarrow Cl_2$; (f) $2IO_4^- \rightarrow I_2$.
3. Does the oxidation state of oxidant increase or decrease in oxidation-reduction reaction? How does the oxidation state of the reductant change in this reaction? Illustrate your answer by examples.
4. Which of the following substances can act only as reductants, or only as oxidants, or both oxidants and reductants?
(a) $KMnO_4$, MnO_2, V_2O_5, KI; (b) PbO_2, NH_3, HNO_2, Na_2S; (c) Na_2SO_3, HNO_3, $K_2Cr_2O_7$, PH_3.
5. Give examples of compounds of nitrogen, chlorine, and manganese where they have only oxidizing or only reducing properties. Write down the formulas for the compounds.
6. Put appropriate coefficients for the following disproportionation reactions:

(a) $HNO_2 \rightarrow HNO_3 + NO + H_2O$
(b) $TiCl_3 \rightarrow TiCl_2 + TiCl_4$
(c) $KOH + Cl_2 \rightarrow KClO + KCl$
(d) $KOH + Cl_2 \rightarrow KClO_3 + KCl$
(e) $K_2MnO_4 \rightarrow KMnO_4 + MnO_2 + KOH$
(f) $Se + KOH \rightarrow K_2SeO_3 + K_2Se + H_2O$
(g) $H_2O_2 \rightarrow H_2O + O_2$

7. Indicate the oxidant and the reductant, and put appropriate coefficients for the following equations of intramolecular oxidation-reduction reactions:

(a) $NH_4NO_2 \rightarrow N_2 + H_2O$
(b) $KClO_3 \rightarrow KCl + O_2$
(c) $Au_2O_3 \rightarrow Au + O_2$
(d) $Pb(NO_3)_2 \rightarrow PbO + NO_2 + O_2$
(e) $(NH_4)_2Cr_2O_7 \rightarrow Cr_2O_3 + N_2 + H_2O$

8. Put appropriate coefficients for the following equations in which the oxidant or the reductant is at the same time the medium where the reaction occurs:

(a) $Zn + H_2SO_4(conc.) \rightarrow ZnSO_4 + H_2S + H_2O$
(b) $Mg + HNO_3 \rightarrow Mg(NO_3)_2 + NH_4NO_3 + H_2O$
(c) $CuS + HNO_3 \rightarrow Cu(NO_3)_2 + SO_2 + NO + H_2O$
(d) $KMnO_4 + HCl\ (conc.) \rightarrow Cl_2 + MnCl_2 + KCl + H_2O$
(e) $K_2Cr_2O_7 + HCl\ (conc.) \rightarrow Cl_2 + CrCl_3 + KCl + H_2O$

9. Decide if the peroxides in the following reactions are oxidants or reductants? Complete the equations and put appropriate coefficients:

(a) $CrCl_3 + H_2O_2 + NaOH \rightarrow Na_2CrO_4 + \ldots$
(b) $KMnO_4 + H_2O_2 + H_2SO_4 \rightarrow MnSO_4 + \ldots$
(c) $Na_2O_2 + KI + H_2SO_4 \leftarrow I_2 + \ldots$
(d) $Mo(NO_3)_3 + Na_2O_2 + NaOH \rightarrow Na_2MoO_4 + \ldots$
(e) $K_2S_2O_8 + MnSO_4 + H_2O \rightarrow MnO_2 + H_2SO_4 + \ldots$

10. Complete the equations and put appropriate coefficients in the following reactions where substances are reduced with organic reductants:

(a) $CuO + C_3H_7OH \rightarrow C_2H_5CHO + H_2O + \ldots$
(b) $KMnO_4 + C_2H_5OH + H_2SO_4 \rightarrow CH_3CHO + \ldots$
(c) $K_2Cr_2O_7 + (COOH)_2 + H_2SO_4 \rightarrow CO_2 + \ldots$
(d) $Ag_2O + C_5H_6(OH)_5CHO \rightarrow C_5H_6(OH)_5COOH + \ldots$

11. Calculate equivalent weights of oxidants and reductants in the following reactions:

(a) $PbO_2 + NaNO_2 + H_2SO_4 \rightarrow PbSO_4 + NaNO_3 + H_2O$
(b) $Cr(OH)_3 + Br_2 + NaOH \rightarrow Na_2CrO_4 + NaBr + H_2O$
(c) $K_2Cr_2O_7 + K_2SO_3 + H_2SO_4 \rightarrow Cr_2(SO_4)_3 + K_2SO_4 + H_2O$
(d) $(NH_4)_6V_{10}O_{28} + KI + HCl \rightarrow VOCl_2 + I_2 + NH_4Cl + KCl + H_2O$

12. Put appropriate coefficients for the following oxidation-reduction reactions:

(a) $As_2O_3 + HNO_3 + H_2O \rightarrow H_3AsO_4 + NO$
(b) $Fe_2(SO_4)_3 + AsH_3 \rightarrow As + FeSO_4 + H_2SO_4$
(c) $KIO_3 + Na_2SO_3 + H_2SO_4 \rightarrow I_2 + Na_2SO_4 + K_2SO_4 + H_2O$
(d) $KMnO_4 + Ca(NO_2)_2 + H_2SO_4 \rightarrow CaSO_4 + Mn(NO_3)_2 + KNO_3 + K_2SO_4 + H_2O$
(e) $As_2O_3 + I_2 + KOH \rightarrow KI + K_3AsO_4 + H_2O$
(f) $Cr_2(SO_4)_3 + Br_2 + KOH \rightarrow K_2CrO_4 + KBr + K_2SO_4 + H_2O$
(g) $KClO_3 + I_2 + H_2O \rightarrow HIO_3 + KCl$
(h) $Zn + HNO_3 \rightarrow Zn(NO_3)_2 + NH_4NO_3 + H_2O$
(i) $Ag + HNO_3 \rightarrow NO_2 + AgNO_3 + H_2O$
(j) $Bi + HNO_3 \rightarrow Bi(NO_3)_3 + NO + H_2O$
(k) $Ca(OH)_2 + Cl_2 \rightarrow Ca(ClO)_2 + CaCl_2 + H_2O$
(l) $K_2Cr_2O_7 + C_2H_4(OH)_2 + H_2SO_4 \rightarrow Cr_2(SO_4)_3 + (COOH)_2 + K_2SO_4 + H_2O$
(m) $V_2S_3 + KMnO_4 + HCl \rightarrow H_6V_{10}O_{28} + S + MnCl_2 + KCl + H_2O$

13. Complete equations for the following oxidation-reduction reactions and put appropriate coefficients in them:

(1) $Zn + H_2SO_4$ (dilute) =
(2) $Zn + H_2SO_4$ (conc.) =
(3) $Al + HNO_3$ (dilute) =
(4) $KMnO_4 + Zn + H_2SO_4 =$
(5) $KMnO_4 + Zn + KOH = K_2MnO_4 + K_2[Zn(OH)_4] + \ldots$
(6) $Cl_2 + I_2 + H_2O =$
(7) $HgO + H_2O_2 = Hg + \ldots$
(8) $Bi_2S_3 + HNO_3 = Bi_2(SO_4)_3 + \ldots$

(9) $K_2Cr_2O_7 + KNO_2 + H_2SO_4 =$
(10) $FeCl_2 + KClO_3 + HCl = FeCl_3 + \ldots$
(11) $H_3AsO_3 + H_2O_2 = H_3AsO_4 + \ldots$
(12) $KClO_4 + Ti_2(SO_4)_3 + H_2O = KCl + TiOSO_4 + \ldots$
(13) $Ca(ClO)_2 + H_2O_2 = CaCl_2 + \ldots$
(14) $KNO_3 + Zn + KOH = NH_3 + K_2[Zn(OH)_4] + \ldots$
(15) $BiCl_3 + SnCl_2 + NaOH = Bi + Na_2[Sn(OH)_6] + \ldots$
(16) $Cr_2(SO_4)_3 + H_2O_2 + KOH = K_2CrO_4 + \ldots$
(17) $NiS + HNO_3 = Ni(NO_3)_3 + S + \ldots$
(18) $ReO_2 + O_2 + NaOH = Na_3ReO_5 + \ldots$
(19) $Co_2O_3 + HCl$ (conc.) $= Cl_2 + \ldots$

14. What quantity (in grams) of crystalline $KMnO_4$ should be taken to prepare 1 litre of a 0.02 *N* solution for oxidation-reduction titration in an acidic medium? The MnO_4^- ion is reduced to Mn^{2+} ion in this reaction.
Answer: 0.63 g.
15. 16 ml of a 0.5 *N* potassium permanganate solution were spent to titrate 20 ml of a solution containing iron(II) sulphate. Calculate the normality and the titre of the iron(II) sulphate solution.
Answer: $N = 0.4$; $T = 0.0608$ g/ml.
16. A piece of iron wire weighing 0.70 g was dissolved in sulphuric acid in the absence of air [to prevent oxidation of iron(II) to iron(III)] in a 100-ml flask. 14.91 ml of a 0.1 *N* potassium permanganate solution were spent to titrate 15 ml of the obtained solution. What is the percentage content of iron in the wire?
Answer: 99.15%.

Examples of Multiple-choice Questions

1. Which of the following substances can act both as the reductant and the oxidant?
(1) $KMnO_4$; (2) KCl; (3) MnO_2; (4) H_2S; (5) $KClO_4$.
2. Which atoms were oxidized in the reaction $Pb(NO_3)_2 \rightarrow PbO + NO_2 + O_2$?
(1) lead; (2) nitrogen; (3) oxygen; (4) lead and nitrogen; (5) nitrogen and oxygen.
3. How many moles of nitric acid act as an oxidant in the reaction $FeS + HNO_3 \rightarrow Fe(NO_3)_3 + S + NO + H_2O$?
(1) 1; (2) 3; (3) 5; (4) 10; (5) 15.
4. What is the sum of the coefficients in the left part of the equation
$FeSO_4 + KMnO_4 + H_2SO_4 \rightarrow Fe_2(SO_4)_3 + MnSO_4 + K_2SO_4 + H_2O$
(1) 10; (2) 13; (3) 18; (4) 20; (5) 26.
5. What fraction of a mole is the equivalent weight of the oxidant in the preceding reaction?
(1) 1 mole; (2) 1/3 mole; (3) 1/7 mole; (4) 1/4 mole; (5) 1/5 mole.

EXPERIMENT 18. OXIDATION-REDUCTION REACTIONS

Apparatus and reagents

Apparatus for preparing hydrogen sulphide. Beaker. Crucible No. 1. Porcelain dish (d = 3-4 cm). Iron strip. Zinc, granules and powder. Sodium. Cerium or mischmetal. Manganese dioxide. Iodine, crystals. Magnesium ribbon. Barium peroxide. Sodium sulphate. Sodium sulphite. Potassium nitrite. Iron sulphide. Copper nitrate $Cu(NO_3)_2 \cdot 3H_2O$. Sodium bismuthate. Ammonium dichromate. Potassium (or ammonium) persulphate. Ethyl alcohol. Solutions: hydrogen sulphide; chlorine water; bromine

water; iodine water; starch; phenolphthalein; oxalic acid, 0.5 *N*; sulphuric acid, 2 *N*, 4 *N*, density 1.84 g/cm^3; hydrochloric acid, 2 *N*, density 1.19 g/cm^3; nitric acid, 0.2 *N*, 2 *N*; acetic acid 2 *N*; sodium hydroxide or potassium hydroxide, 2 *N*; ammonium hydroxide, 2 *N*, 25%; manganese sulphate, 0.5 *N*; copper sulphate, 0.5 *N*; sodium sulphite, 0.5 *N*; tin(II) chloride, 0.5 *N*; potassium dichromate, 0.5 *N*; potassium permanganate, 0.5 *N*; mercury(II) nitrate, 0.5 *N*; silver nitrate, 0.1 *N*; formaldehyde, 10% solution; hydrogen peroxide, 3% solution; potassium iodide, 0.5 *N*; zinc sulphate, 0.5 *N*; iron(III) chloride, 0.5 *N*; potassium ferricyanide, 0.5 *N*; titanium(IV) salt, 0.5 *N*; sodium (or ammonium) sulphide, 0.5 *N*; sodium hydroxide, 2 *N*.

1. Reducing Properties of *s*, *d*, and *f* Elements*

Procedure. Place 3-5 ml of distilled water in a small porcelain dish. Obtain from the laboratory assistant a small grain of sodium metal on a filter paper, dry the sodium with the paper, and drop into water. What gas is liberated? Add 1-2 drops of phenolphthalein: why does the solution become coloured?

Repeat the experiment using a grain of cerium or mischmetal (a mixture of rare-earth elements) instead of sodium. If the reaction is slow, add a few drops of a 4 *N* sulphuric acid solution. Turbidity (in the absence of the acid) is due to poor solubility of cerium oxide and cerium hydroxide in water, which are otherwise dissolved in sulphuric acid.

Place 10-12 drops of copper(II) sulphate solution into one test tube and the same amount of zinc sulphate solution into another test tube. Place iron strips into both. Why does a red film appear on the iron surface in copper(II) sulphate solution in 2-3 minutes? Add 2-3 drops of potassium ferricyanide $K_3[Fe(CN)_6]$ into the first test tube: an intense blue colour develops to indicate the appearance of the Fe^{2+} ion in the solution. Add potassium ferricyanide to the other solution. Does iron react with zinc sulphate?

Recording the results. Write down the equations for reactions of sodium and cerium with water, and of iron with copper(II) sulphate.

What properties (oxidizing or reducing) do sodium, cerium and iron demonstrate in these reactions? Why does iron not displace zinc from its salt?

What elements (*s*, *p*, *d*, or *f*) are sodium, cerium and iron? Write

* Some *p* elements as simple substances also have reducing properties and are therefore attributed to metals.

down the electron structures of these elements and explain why they cannot act as oxidants in the free state?

2. Oxidizing and Reducing Properties of Simple Substances of *p* Elements*

A. Oxidizing and reducing properties of molecular halogens

Procedure. Place 3-4 drops of iodine water into each of two test tubes. Add a few drops of chlorine water to one test tube and of hydrogen sulphide solution to the other. Observe the colour change in the solutions.

Recording the results. Write down the equations for the reactions taking into account that hydrochloric acid and iodic acid HIO_3 are formed in the first test tube. Turbidity of solution in the second test tube is explained by liberation of colloidal sulphur, which is among the reaction products.

Which halogen is an oxidant and which is a reductant in these reactions? What negative oxidation state display these halogens in their compounds? What is their highest positive oxidation state?

B. Oxidizing and reducing properties of sulphur

Procedure. (Use the hood.) Place 4-5 microspatulas of powdered zinc and sulphur into a crucible and heat over the flame of a burner to sinter the powders. Cool the crucible, transfer the contents onto a piece of filter paper. Take a piece of the formed zinc sulphide. Place it in a test tube and add 2 *N* hydrochloric acid solution. Smell the evolving gas and identify it.

Recording the results. Write down the equation for the reaction between zinc and sulphur. What is the oxidation state of sulphur in the obtained compound? Sulphur burns in air to form sulphur dioxide. What is the oxidation state of sulphur in SO_2? What properties (oxidizing or reducing) has free sulphur in each case? Pay attention to the dualism of the oxidation-reduction properties of *p* elements in the form of simple substances.

3. Reducing Properties of *p* Elements in Their Negative Oxidation State

Procedure. Place 2-3 drops of bromine water into each of two test tubes. Add a few drops of hydrogen sulphide solution to one test tube and a 25% ammonia solution to the other. Observe the colour change in the solutions.

* Exceptions are the noble gases, *p* elements of group IIIA, which have no oxidizing properties when in the free state, and also oxygen and fluorine which have no reducing properties.

Write down the equations for the reactions taking into consideration that sulphur is among the products of the reaction between bromine and hydrogen sulphide, and that nitrogen is liberated from ammonia in the second reaction. What properties display sulphur(—II) and nitrogen(—III) in these oxidation-reduction reactions?

Place 2-3 drops of potassium iodide into a clean test tube and add chlorine water. What substance accounts for the developing brown colour of the solution? Write down the reaction equation. What role does I^- ion play in this oxidation-reduction reaction?

Write down the electron structures of the atoms of iodine, sulphur and nitrogen in their negative oxidation states. Can these atoms act as oxidants in chemical reactions?

4. Oxidizing Properties of Elements in Their Higher Oxidation State

Procedure. Write down the electron structures of the atoms of sulphur, chromium, bismuth and titanium in their higher oxidation states and decide if these atoms act as oxidants (reductants) in chemical reactions. To prove your answers, conduct the following experiments.

Place 3-4 drops of hydrogen sulphide solution into each of four test tubes. Add 2-3 drops of concentrated sulphuric acid (density 1.84 g/cm^3) into the first test tube. The developing turbidity is explained by liberation of sulphur in the interaction between S^{-II} and S^{+VI}. What properties does sulphur demonstrate in each of these oxidation states? Write down the reaction equations.

Add 3-4 drops of 2 *N* hydrochloric acid into another test tube. Explain the absence of any precipitate. Add 1-2 drops of potassium dichromate $K_2Cr_2O_7$ until the solution colours green, the colour specific for Cr^{3+} ion. The solution turns cloudy, why? Write down the reaction equation and indicate the reductant and the oxidant.

Place 2-3 drops of a manganese(II) sulphate solution into the third test tube and add 2-3 drops of a 2 *N* nitric acid solution and a microspatula of sodium bismuthate $NaBiO_3$. The solution turns violet which indicates that Mn^{2+} ion is oxidized with sodium bismuthate to the permanganate ion MnO_4^-. Write down the reaction equation bearing in mind that permanganic acid and bismuth(III) nitrate are the products of the oxidation-reduction reaction.

Place 4-5 drops of titanium(IV) oxysulphate solution into the fourth test tube and add 2-3 drops of 4 *N* sulphuric acid solution and a grain of zinc. The violet colour indicates reduction of titanium(IV) to titanium(III). Write down the reaction equation and indicate the transfer of the electrons. Have you thus proved your suggestions experimentally?

5. Oxidizing and Reducing Properties of *p* and *d* Elements in the Intermediate Oxidation States

A. Sulphur(+IV) compounds

Procedure. Place potassium dichromate $K_2Cr_2O_7$ solution into one test tube and sodium sulphide Na_2S solution into another. Add a few drops of 2 *N* sulphuric acid and 2-3 microspatulas of sodium sulphite Na_2SO_3 to each test tube. How does the colour change in the first test tube? Explain why the solution in the second test tube turns cloudy. Do $K_2Cr_2O_7$ and Na_2S act as oxidants or reductants in chemical reactions? Which properties (oxidizing or reducing) does Na_2SO_3 exhibit? Write down the equations for the reactions.

B. Tin(II) compounds

Procedure. Place 2-3 drops of iron(III) chloride and of potassium ferricyanide solution into a test tube. Note the colour of the mixture and add a few drops of tin(II) chloride solution. The developing intense blue colour indicates the presence of Fe^{2+} ions that form a blue precipitate with $K_3[Fe(CN)_6]$. Tin(II) chloride converts into tin(IV) chloride in this reaction.

Place 5-6 drops of tin(II) chloride into another test tube and add a grain of zinc: observe deposition of lustrous tin crystals on the surface of the zinc grain.

Write down the equation for the reactions between tin(II) chloride and iron(III) chloride, and between tin(II) chloride and zinc. Does Sn^{2+} ion act as an oxidant or reductant in these reactions?

6. Variation of Oxidation-reduction Properties of Elements with Their Oxidation State

Procedure. Use sulphur compounds for your experiments.

Place 3 drops of potassium permanganate and of 2 *N* acetic acid (to create an acidic medium) into each of three test tubes. Add 3 drops of a freshly prepared hydrogen sulphide water into the first test tube, a few crystals of sodium sulphite into the second, and 3 drops of concentrated sulphuric acid (density 1.84 g/cm^3) to the third test tube.

Note in which test tube the colour of potassium permanganate vanishes. Write down the equations for the reactions if it is known that potassium permanganate converts into a manganese(II) salt in an acidic medium. What properties do sulphur compounds exhibit in these reactions? Why does the colour of potassium permanganate remain unchanged in one test tube?

Try if H_2S and H_2SO_4 react with potassium iodide. To do this, place 3 drops of a potassium iodide solution into each of two test tubes. Add 2-3 drops of concentrated sulphuric acid to one test tube and the same amount of hydrogen sulphide solution to the other.

In order to prove that the yellow colour is due to the presence of iodine, add 2-3 drops of fresh starch solution and observe it turning blue. Write down the reaction equation.

Why does iodine not evolve in one of the test tubes?

In order to draw a final conclusion on the oxidation or reduction properties of sulphur in various oxidation states carry out the following experiment. Place a microspatula of sodium sulphite crystals into a test tube and add 5-6 drops of 2 *N* sulphuric acid solution. After dissolution is complete, pass hydrogen sulphide through the solution until sulphur precipitates (*use the hood*!). Write down the equation for the reaction of sulphur dioxide, formed during dissolution of sodium sulphite in sulphuric acid, with hydrogen sulphide.

Write down the equations for all reactions. Draw a conclusion on the changes in the oxidizing and reducing properties of sulphur with changing of its oxidation state.

7. Reaction of Disproportionation (Auto-oxidation-reduction)

A. Disproportionation of sodium sulphite

Procedure. Place 2-3 crystals of sodium sulphite into each of two test tubes and save one as a reference. Fix the other test tube in a stand and heat for 5-6 minutes. Allow the test tube to cool and add 5-6 drops of distilled water to both test tubes. Stir the contents using glass rods to dissolve the salts. Add 2-3 drops of copper(II) sulphate solution into each test tube: note the colour of the precipitates.

Recording the results. Explain the different colour of the precipitates. The black precipitate in the second test tube is copper sulphide. What product of sodium sulphite calcining reacts with copper sulphate to give this precipitate?

Write down the equation for the reaction of sodium sulphite decomposition bearing in mind that the other product of decomposition is sodium sulphate. How does the oxidation state of sulphur change in this reaction? Which oxidation states of sulphur are involved in disproportionation reactions?

B. Disproportionation of bromine

Procedure. Place 5-7 drops of bromine water into a test tube and add, drop by drop, 2 *N* alkali solution until the solution is decolourized.

Write down the equation for the reaction between bromine and alkali bearing in mind that salts of hydrobromic acid and hypobromic

acid HBrO are formed. Indicate the changes in the oxidation state of bromine. What reactions are called disproportionation?

8. Intramolecular Oxidation-reduction Reactoins

A. Decomposition of copper nitrate

Procedure. Place a few crystals of copper nitrate $Cu(NO_3)_2 \cdot 3H_2O$ in a test tube. Fix the tube in the stand, and heat carefully over a small flame of the burner.

Observe the colour change of the salt and liberation of a gas.

Recording the results. Write down the equation for the reaction of decomposition of copper nitrate bearing in mind that the reaction products are copper oxide, nitrogen dioxide, and oxygen. Indicate the oxidant and the reductant in the copper nitrate molecule. Draw up the electron transfer diagram.

B. Decomposition of ammonium dichromate

Procedure. Place a few microspatulas of crystalline ammonium dichromate $(NH_4)_2Cr_2O_7$ in a heap in a porcelain dish. Put a ribbon of magnesium into the heap and light it up. Observe a vigorous decomposition of the salt.

Write down the equation for the reaction taking into account the fact that the green grains are chromium(III) oxide. Nitrogen and water vapour are other reaction products. Which element acts as oxidant in this reaction? Which element acts as a reductant? How do oxidation states of these elements change?

9. Effect of Medium on Oxidation-reduction Reactions

A. Effect of pH on reduction of potassium permanganate

Procedure. Place 3-4 drops of potassium permanganate solution into three test tubes. Add 2-3 drops of 2 *N* sulphuric acid solution into one test tube, the same amount of water into the other, and of an alkali solution to the third test tube. Add two microspatulas of potassium nitrite crystals to each of three test tubes and stir the solutions to complete dissolution of the crystals. In 3-4 minutes, observe the colour change in all three test tubes.

Recording the results. Write down the equations for the reaction of potassium permanganate reduction with potassium nitrite in an acidic, neutral and alkaline medium. Take into account that the compounds of manganese in its various oxidation states are coloured in different hues: MnO_4^- ion is violet, MnO_4^{2-} ion is green, and Mn^{2+} ion is pale pink (practically colourless in small concentration).

Manganese dioxide and manganese hydroxide are sparingly soluble brown substances. Gaseous nitrogen oxides are the products of a side reaction of potassium nitrite and sulphuric acid, and can therefore liberate in an acidic medium.

To what oxidation state is the permanganate reduced in solutions whose pH is lower than 7, equal to 7, or higher than 7? How many oxidation equivalents does 1 mole of $KMnO_4$ contain in each case?

B. Effect of pH on equilibrium in disproportionation reactions

Procedure. Place a small crystal of iodine into a test tube and add 8-10 drops of 2 *N* alkali solution. Stir the mixture to dissolve iodine. Add 10-14 drops of 2 *N* sulphuric acid to the obtained colourless solution until it turns brown. Using a starch solution, show that the brown colour is due to the reverse reaction of formation of free iodine.

Recording the results. Salts of hydriodic and iodic (HIO) acids are formed during dissolution of iodine in alkali solution. Write down the net ionic equation for the oxidation-reduction reaction and explain the liberation of free iodine when the solution is acidified.

10. Oxidizing and Reducing Properties of Peroxides

A. Disproportionation of hydrogen peroxide

Procedure. Place a few drops of hydrogen peroxide in a test tube and add 2 *N* sulphuric acid solution. What gas evolves?

Write down the reaction of hydrogen peroxide disproportionation with formation of oxygen and water. Put the appropriate coefficients (by the half-reaction method):

for the reaction of hydrogen peroxide reduction (H_2O_2 is oxidant)

$$H_2O_2 + 2H^+ + 2e^- = 2H_2O$$

for the reaction of hydrogen peroxide oxidation (H_2O_2 is reductant)

$$H_2O_2 - 2e^- = O_2 + 2H^+$$

B. Reaction of hydrogen peroxide with potassium iodide

Procedure. Add 1-2 drops of hydrogen peroxide solution to a potassium iodide solution acidified with sulphuric acid. What substance accounts for the developing colour of the solution?

Write down the reaction equation. Does hydrogen peroxide act as a reductant or oxidant in this reaction?

C. Reaction of hydrogen peroxide with mercury(II) oxide

Procedure. Place 3-4 drops of mercury nitrate $Hg(NO_3)_2$ solution into a test tube and add the same amount of 2 *N* alkali solution to precipitate mercury (II) oxide. Note the colour of the precipitate. Add 4-5 drops of hydrogen peroxide solution and observe the change of the precipitate colour due to formation of suspended particles of metal mercury. What gas liberates in the reaction?

Write down the reaction equation. Does hydrogen peroxide act as a reductant or oxidant in this reaction?

D. Reaction of barium peroxide with potassium permanganate

Procedure. Place a few drops of potassium permanganate solution into a test tube and add 1-2 microspatulas of barium peroxide BaO_2. How does the solution colour change? What gas is liberated?

Write down the reaction equation bearing in mind that the precipitated brown flakes are manganese dioxide. Does barium peroxide act as an oxidant or reductant in this reaction? Draw structural formulas of manganese dioxide and barium peroxide.

E. Reaction of potassium (ammonium) persulphate with chromium(III) sulphate

Procedure. Place 3-4 drops of a chromium(III) salt solution into a test tube, add 2-3 drops of sulphuric acid and 1-2 drops of silver nitrate (catalyst), and heat over a small flame of a burner. Add 2-3 crystals of potassium persulphate $K_2S_2O_8$ (or ammonium persulphate) into the hot solution and heat again until the colour changes.

Recording the results. Draw a structural formula of potassium (ammonium) persulphate. Put the appropriate coefficients in the reaction equation, and indicate the oxidant and the reductant:

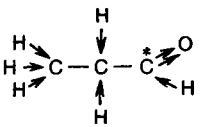
$$Cr_2(SO_4)_3 + (NH_4)_2S_2O_8 + H_2O \rightarrow (NH_4)_2SO_4 + (NH_4)_2Cr_2O_7 + H_2SO_4$$

11. Organic Substances in Oxidation-reduction Reactions

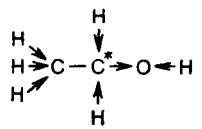
Many organic substances are used as reductants in oxidation-reduction reactions. Not all carbon atoms of the organic molecule change their oxidation state (act as reductants), but only those in the functional group, or those directly connected to it.

The coefficients in the reaction equations should be selected by the electron balance. The conventional oxidation state of the reducing carbon atom is calculated by assuming that electron pairs are drawn to the more electronegative elements, while electronegativities of carbon, hydrogen and oxygen decrease in the series oxygen—carbon—hydrogen. It follows that the chemical bond between the

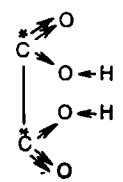
carbon atoms is nonpolar. In a polar carbon-oxygen bond, the carbon atom is polarized positively and acquires a conventionally positive charge in a single bond $C^{+I} \rightarrow 0$; in a double bond, it acquires two positive charges $C^{+II} \rightrightarrows 0$; the carbon atom in the C—H bond is polarized negatively and acquires one negative charge $C^{-I} \leftarrow H$. The oxidation state of a reducing carbon atom in a compound is calculated as an algebraic sum of conventionally acquired positive and negative charges. For example, in a molecule of propionic aldehyde C_2H_5CHO, with the structural formula



the carbon atom marked by an asterisk is the reductant. Its oxidation state is $0 + II - I = + I$. In the molecule of ethyl alcohol



the oxidation state of the reducing carbon atom is —I. In the molecule of oxalic acid



both carbon atoms act as reductants; the oxidation state of each atom is + III.

The coefficients for the equations of reactions where an organic substance is oxidant are selected in a similar way.

A. Reduction of potassium dichromate with alcohol

Procedure. Place 5-6 drops of potassium dichromate solution into a test tube and add 2-3 drops of concentrated sulphuric acid (density 1.84 g/cm^3) and 4-5 drops of ethyl alcohol C_2H_5OH. Note the colour change and appearance of odour of an apple which is specific for acetaldehyde CH_3CHO.

Write down the reaction equation taking into account the fact that chromium(VI) is reduced to chromium(III).

B. Reduction of ammonia solution of silver nitrate with formaldehyde

Procedure. Boil 25-50 ml of water in a small beaker. Add 4-5 drops of silver nitrate solution and 3-5 drops of 2 *N* ammonia solution. Shake the test tube after adding each new drop of ammonia solution until the Ag_2O precipitate is dissolved (avoid excess NH_3). Add 10% formaldehyde solution to the clear solution. (The volume of formaldehyde should be equal to the sum of the volumes of silver nitrate and ammonia solution.) Stir the solution and place the test tube in a beaker with hot water for 2-3 minutes. Remove the test tube from the beaker, discard the solution, rinse the test tube with water from a wash bottle and observe a silver mirror on the internal walls of the test tube that were in contact with the solution.

Write the reaction equation assuming that formaldehyde is oxidized to formic acid HCOOH in the reaction with silver oxide.

C. Reduction of potassium permanganate with oxalic acid

Procedure. Place 5-6 drops of oxalic acid $H_2C_2O_4$ in a test tube and add the same amount of 2 *N* hydrochloric acid. Heat the solution in the test tube to 70-80 °C in a beaker with hot water for 4-5 minutes. Remove the test tube from hot water and add a few drops of potassium permanganate solution. Shake the solution after adding each next drop. Observe decolourization of potassium permanganate due to its reduction to manganese(II), and evolution of carbon dioxide formed due to oxidation of oxalic acid. Write down the reaction equation. How many electrons does the molecule of oxalic acid give off?

EXPERIMENT 19. QUANTITATIVE DETERMINATION OF SUBSTANCES BY OXIDATION-REDUCTION TITRATION

Apparatus and reagents

Burette. Pipette. Volumetric flasks, 100-ml. Pipettes, 15-20 ml. Funnel. Solutions: potassium permanganate, 0.05 *M*; hydrogen peroxide, 3%; iron(II) sulphate, 0.05 *M*; sulphuric acid, 2 *N* and 4 *N*; ortho-phosphoric acid, 4 *N*.

Permanganatometric titration is a method of oxidation-reduction titration based on oxidation of reductants with potassium permanganate. Titration is usually carried out in an acidic medium, because in an acidic medium MnO_4^- ion that colours solution pink is reduced to a colourless Mn^{2+} ion. The point of equivalence can thus be easily

located without using any indicators. Moreover, the oxidizing power of permanganate in an acidic medium is much higher and hence the field of its application is wider than in a neutral or alkaline media.

1. Determining Concentration of Hydrogen Peroxide in Solution

Procedure. Weigh a dry weighing bottle on an analytical balance to an accuracy of 0.0002 g and transfer the test solution of hydrogen peroxide (obtained from the instructor) into it. Weigh the bottle with the solution to the same accuracy. Transfer the weighed solution into a 100-ml volumetric flask, if the hydrogen peroxide solution weighs about 3 g. If its weight is greater, take a larger flask. Transfer the solution carefully, pouring it along a glass rod into a funnel put into the neck of a volumetric flask. Rinse the weighing bottle and the glass rod several times with small portions of distilled water, transfer the washings into the flask. Stir its contents by rotating the flask, and add water to the mark. Close the flask with a stopper, and overturn several times.

Place a standard 0.05 *N* potassium permanganate solution into a dry beaker, rinse a burette with this solution, and fill the burette (fixed in the stand) with the solution to the level above zero reading. See to it that the burette tip is filled with the solution (no air bubbles should be present). Adjust the potassium permanganate level in the burette to zero by the upper edge of the meniscus (as in titration with coloured solutions).

Using a 15-20 ml pipette, transfer the hydrogen peroxide solution from the volumetric flask into an Erlenmeyer flask and add 5-10 ml of 2 *N* sulphuric acid solution. Carry out tentative titration. To do so, add potassium permanganate solution from the burette into the acidified colourless hydrogen peroxide solution by small (0.5 ml) portions. Stir the solution by circular movements after adding each new portion until the pink colour, which first develops, vanishes. Continue the titration until the solution turns pale pink from a drop of the potassium permanganate solution and remains so for 30 seconds. Note the volume of the permanganate solution spent for titration. Now carry out three accurate titrations. Approaching the end of titration add the potassium permanganate by drops. The deviations between the measured volumes of potassium permanganate solution should not exceed 0.05 ml. Use the mean volume of the three last titrations for calculations.

Recording the results and calculations. Write down your findings into the log-book.

Weight of the weighing bottle, m_1, g.

Weight of the weighing bottle with hydrogen peroxide, m_2, g.

Weight of hydrogen peroxide solution, $m_3 = m_2 - m_1$, g.
Volume of volumetric flask, V_f, ml.
Volume of pipette, $V_{H_2O_2}$, ml.
Volume of potassium permanganate solution spent for titration: V_1, ml; V_2, ml; V_3, ml; mean V_{KMnO_4}, ml.

The quantitative determination of hydrogen peroxide is based on the reaction:

$$5H_2O_2 + 2MnO_4^- + 6H^+ \rightarrow 5O_2 + 2Mn^{2+} + 8H_2O$$

Use the results of titration to calculate the normality of the solution in the volumetric flask from the following equation:

$$V_{KMnO_4} N_{KMnO_4} = V_{H_2O_2} N_{H_2O_2}$$

The H_2O_2 molecule gives off two electrons, hence the equivalent mass $Eq_{H_2O_2} = M/2 = 17$ g.

Determine the mass (in grams) of H_2O_2 in the sample, i.e. in the volume of the volumetric flask, using the formula

$$m_{H_2O_2} = \frac{17 N_{H_2O_2} \times V_f}{1000}$$

Calculate the hydrogen peroxide concentration (in %) in the test solution:

$$c_{H_2O_2} = \frac{m_{H_2O_2} \times 100}{m_3}$$

Let the instructor check your results.

2. Determining Iron in Solution of Its Salt

The determination of iron and its compounds is based on titration of solutions containing Fe^{2+} ions with potassium permanganate solution of known concentration (standard solution).

The reaction proceeds according to this equation:

$$MnO_4^- + 5Fe^{2+} + 8H^+ \rightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$$

If iron is determined in a solution containing both Fe^{2+} and Fe^{3+} ions, the latter are first reduced to iron(II). This method is used, for example, during the analysis of cast iron, steels, or iron ores after their dissolution in H_2SO_4. Preparation of solutions containing Fe^{2+} ions, and the titration process itself, should be carried out as quickly as possible in order to decrease the time during which the solutions are in contact with atmospheric oxygen.

Procedure. Obtain an accurately measured volume of the test iron(II) sulphate solution from the instructor (in a 100-200-ml flask). Add 10 ml of 4 *N* sulphuric acid and dilute the obtained solution with distilled water to half the flask capacity. It is also recommended

to add 5-10 ml of phosphoric acid, which reacts with Fe^{3+} ions, formed during the titration process, to give a colourless complex compound, which in turn colours the solution pink at the end of titration. If phosphoric acid is not available, the yellow colour of the solution changes to pink at the end of titration. This change in hue is however not so obvious.

Rotate the flask to stir the solution and add water to the mark. Stir thoroughly again the obtained solution.

Fill a burette with 0.05 N potassium permanganate solution and adjust the solution level at zero.

Carry out a tentative titration of the test solution. To do so, pipette 10-20 ml of the solution from the volumetric flask into an Erlenmeyer flask and add, in small portions, the potassium permanganate solution from the burette until the solution turns pale pink and remains so for at least 30 seconds. The first drops of the potassium permanganate solution are decolourized slowly, but as a small quantity of Mn^{2+} ions is formed in the solution, they act as a catalyst and the further decolourization of the permanganate solution occurs almost instantaneously. Carry out three accurate titrations, and find the mean volume from the three results that differ by not more than 0.05 ml.

Recording the results and calculations. Write down the results of the experiment in the log-book.

Volume of the test solution obtained from the instructor, V, ml.

Volume of the flask with the test solution, V_f, ml.

Volume of the pipette, V_p, ml.

Volume of potassium permanganate solution spent for titration: V_1, V_2, V_3, mean $V_{KMnO_4,m}$ (in ml).

Use these findings in your calculations.

Calculate the normality of the $FeSO_4$ test solution, and the concentration of Fe^{2+} ions, in g/l. To do so, calculate the volume of 0.05 N solution of potassium permanganate (in ml) spent for oxidation of Fe^{2+} ions in the volume V of the solution obtained from the instructor (i.e. in the volume of the volumetric flask):

$$V_{KMnO_4} = \frac{V_{KMnO_4,m} V_f}{V_p}$$

Calculate the normality N_x of the test solution from the rule of equivalence of the oxidant and the reductant:

$$VN_x = V_{KMnO_4} N_{KMnO_4} = V_{FeSO_4} N_{FeSO_4}$$

Calculate the concentration of Fe^{2+} ions in the test solution (in g/l). To what quantity of metallic iron does this content of Fe^{2+} ions correspond?

10 Electrochemical Processes

QUESTIONS AND PROBLEMS

1*. Write down the molecular and ionic equations for possible reactions of metal displacement from their salts by other metals and use an arrow to indicate the electron transfer:

(a) $Zn(NO_3)_2 + Pb$
(b) $AlCl_3 + Mg$
(c) $AgNO_3 + Cu$
(d) $FeSO_4 + Zn$
(e) $Pb(NO_3)_2 + Ag$
(f) H_2SO_4(dil.) + Ni
(g) HCl (dil.) + Cu
(h) $Na_2SO_4 + Al$

2. Chemically pure zinc almost does not react with hydrochloric acid. If a nickel salt is added, the reaction proceeds vigorously with liberation of hydrogen. Explain these phenomena.

3. Draw up diagrams of voltaic cells for the determination of the standard potentials for the Ni^{2+}/Ni and Cu^{2+}/Cu electrodes in couples with the standard hydrogen electrode. Indicate the electron transfer in the external circuit.

4. Draw up diagrams for two voltaic cells in one of which nickel is anode and in the other, cathode. Write down the equations for the processes occurring at the nickel electrodes during the work of the cells.

5. Draw up a diagram for a voltaic cell consisting of a cobalt and an iron plates immersed in 1 *M* solutions of cobalt and iron sulphites. Indicate the direction of electron transfer in the circuit and of the ions in the solution. Write down the equations for the reactions occurring at the cathode and anode in the cell and calculate its e.m.f.
Answer: 1.94 V.

6. Calculate the e.m.f. of a copper-zinc voltaic cell working with the electrolytes of the following concentrations: 1.5 *M* $CuSO_4$ and 0.01 *M* $ZnSO_4$.
Answer: 1.163 V.

7. Calculate the e.m.f. of a concentration voltaic cell made up of two copper electrodes, one of which is immersed in 0.001 *M* $CuSO_4$ and the other in 1 *M* $CuSO_4$ solution.
Answer: 0.087 V.

8. Which half-cells should be taken to compose a voltaic cell with the maximum e.m.f.: (1) Ca^{2+}/Ca and Au^{3+}/Au; (2) Zn^{2+}/Zn and Fe^{2+}/Fe; (3) Ni^{2+}/Ni and Pb^{2+}/Pb; (4) Mg^{2+}/Mg and Cd^{2+}/Cd; (5) Fe^{2+}/Fe and Ni^{2+}/Ni?

9. Which half-cells make up a voltaic cell with the maximum e.m.f.: (1) Cu^{2+}/Cu and Pb^{2+}/Pb; (2) Cr^{3+}/Cr and Fe^{2+}/Fe; (3) Pb^{2+}/Pb and Cr^{3+}/Cr; (4) Cr^{3+}/Cr and Cu^{2+}/Cu; (5) Pb^{2+}/Pb and Fe^{2+}/Fe?

10. If a protective coat is damaged, iron is corroded faster in which case:
(a) tin- or zinc-plated iron?
(b) chromium- or nickel-plated iron? Explain your answer.

11. Write down half-reactions in the following oxidation-reduction system:

$$KIO_3 + FeSO_4 + H_2SO_4 \rightarrow I_2 + Fe_2(SO_4)_3 + K_2SO_4 + H_2O$$

Indicate the direction of the process and calculate the e.m.f. of the oxidation-reduction cell employing this reaction.
Answer: 0.42 V.

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* When solving Problems Nos. 1 through 15, consult Table 11 of Appendix to find the values of standard electrode potentials. Unless specified in the problem, the concentrations of the oxidant and the reductant are assumed to be 1 mole ion per litre.

12. In what direction (forward or reverse) will the following oxidation-reduction reactions proceed at STP? or the system will be at equilibrium?

$KMnO_4 + Br_2 + H_2SO_4 \rightleftarrows MnSO_4 + KBrO_3 + H_2O$
$KBrO_3 + KAsO_2 + KOH \rightleftarrows K_3AsO_4 + KBr + H_2O$
$KIO_3 + H_2O + SO_2 \rightleftarrows I_2 + H_2SO_4 + K_2SO_4$
$NaI + Na_2SO_4 + H_2O \rightleftarrows I_2 + Na_2SO_3 + NaOH$
$MnSO_4 + PbO_2 + HNO_3 \rightleftarrows HMnO_4 + PbSO_4 + Pb(NO_{3/2} + H_2O$
$K_2Cr_2O_7 + NaCl + H_2SO_4 \rightleftarrows Cr_2(SO_4)_3 + Cl_2 + Na_2SO_4 + K_2SO_4 + [H_2O$

13. Which of the following oxidants: $KMnO_4$, $K_2Cr_2O_7$, or I_2 (the first two oxidants in an acidic medium) will oxidize chloride ion Cl^-?
14. Which of the halide ions (F^-, Cl^-, Br^-, or I^-) will be oxidized with Fe^{3+} ion according to the diagram: $Fe^{3+} + Hal^- \rightarrow Fe^{2+} + Hal_2$?
15. Which of the following oxidation-reduction pairs will reduce iron(III) to iron(II)?
(a) IO_3^-/I_2; (b) PbO_2/Pb^{2+}; (c) Co^{3+}/Co^{2+}; (d) $Br_2/2Br^-$; (e) $I_2/2I^-$.
16. Write down the equations for the cathode and anode reactions occurring during electrolysis of aqueous solutions of the following substances with graphite electrodes: (a) nickel chloride; (b) calcium nitrate; (c) sodium hydroxide; (d) iron(II) sulphate; (e) sulphuric acid; (f) silver nitrate.
17. What products will be liberated at first at the cathode and anode during electrolysis of aqueous solutions, if mixtures of the following salts are present in the electrolyzer:
(a) $CuSO_4$ and KCl; (b) $NiSO_4$ and NaCl; (c) $FeCl_3$ and Na_2SO_4; (d) $SnCl_2$ and KI?
18. Write down equations for the reactions occurring at the electrodes during electrolysis of the following solutions: (a) nickel sulphate with nickel electrodes; (b) silver nitrate with silver electrodes; (c) copper chloride with copper electrodes.
19. Current passes successively through solutions of copper sulphate and tin(II) chloride. During a certain period of time, 3.176 g of copper are precipitated in the first solution. Determine the mass of the precipitated tin and the theoretical volume of chlorine gas liberated at STP.
Answer: 5.93 g of tin and 1.12 litres of chlorine.
20. Current of 1.5 A passes successively through solutions of iron(II) sulphate and iron(III) chloride during one hour. Determine the mass of iron deposited in each bath.
Answer: 1.56 g and 1.04 g.
21. As a current of 5 A passes through an electrolyte solution during a period of 2 hours 2 minutes and 2 seconds, 12.4 g of metal are deposited. Determine the equivalent mass of the metal and the electrochemical equivalent.
Answer: 32.7 g; 0.00034 g.
22. During what time should a current of 5 A be passed through a solution of an electrolyte to deposit a chemical equivalent of any metal, or an electrochemical equivalent of any metal?
Answer: 5 hours 22 minutes; 0.2 second.
23. As a current of 0.5 A passes through an electrolyte solution for an hour, it deposits 0.55 g of a metal. Determine the electrochemical equivalent and an equivalent mass of the metal.
Answer: 0.00031 g; 29.43 g.
24. As a current of 2 A passes through an electrolyte solution during 44 minutes, 2.3 g of a metal deposits. Determine the equivalent mass and the electrochemical equivalent of this metal.
Answer: 56.16 g; 0.0006 g.
25. Calculate the electrochemical equivalent of iron in the following compounds: (a) $FeSO_4$, and (b) $Fe_2(SO_4)_3$.
Answer: (a) 0.0003 g; (b) 0.0002 g.

Examples of Multiple-choice Questions

1. Consult the table of standard electrode potentials of metals to indicate a correct e.m.f. for a voltaic cell with the Fe^{2+}/Fe and Ni^{2+}/Ni electrodes:
(1) −0.19; (2) +0.19; (3) −0.69; (4) +0.69; (5) −0.47.
2. Decide if the following oxidation-reduction process is possible at STP? If yes, then in what direction?

$$KMnO_4 + Br_2 + H_2SO_4 \rightarrow KBrO_3 + MnSO_4 + H_2O$$

(1) possible in the forward direction; (2) possible in reverse direction; (3) impossible.
3. Which of the following oxidants can oxidize iron(II) to iron(III)?
(1) $KMnO_4$ in a neutral medium; (2) $KMnO_4$ in an acidic medium; (3) Br_2, with reduction to Br^- ions; (4) Cl_2, with reduction to Cl^- ions; (5) I_2, with reduction to I^- ions.
4. What substance will liberate at the cathode during electrolysis of an aqueous solution of $CrCl_3$ and NaBr?
(1) Na; (2) H_2; (3) Cl_2; (4) Cr; (5) O_2.
5. What substance will liberate at the anode during electrolysis of an aqueous solution of $NiCl_2$ with a nickel anode?
(1) Cl^-; (2) Ni^{2+}; (3) Ni; (4) H_2O.

EXPERIMENT 20. DETERMINING ELECTRODE POTENTIALS. DIRECTION OF OXIDATION-REDUCTION PROCESSES

Apparatus and reagents

Galvanometer. pH-meter (millivoltmeter). Base plate for a voltaic cell. Salt bridge. Flash-light cell. Beakers, 50-ml. Electric wire. Copper, iron, and platinum wires. Zinc (plate and pure granules). Copper (pieces). Tin, granules. Lead (plate). Emery paper. Phenolphthalein. Solutions. iodine water; zinc sulphate, 1 *M* and 0.01 *M*; copper sulphate, 1 *M*; potassium chloride, 1 *N*, saturated; sulphuric acid, 2 *N*, 3.5 *M*; potassium sulphate, 1 *N*; chromium(III) sulphate, 0.5 *M*; potassium dichromate, 0.5 *M*; potassium ferricyanide, 0.5 *N*; mixture of $SnCl_2$ and $SnCl_4$ (1 mole of each in 1 litre of solution); mixture of $FeCl_2$ and $FeCl_3$ (1 mole of each in 1 litre of solution).

1. Composing a Voltaic Cell

A. Copper-zinc cell

Procedure. Fill one beaker *1* (Fig. 37) with 1 *M* zinc sulphate solution (in which the activity of the metal ions is unity) and another beaker with 1 *M* copper sulphate solution. Place the beakers in the recesses in the base plate *2*. Connect the beakers by means of a salt bridge *3* filled with a saturated solution of potassium chloride mixed with agar-agar. Immerse a zinc plate into the zinc sulphate solution

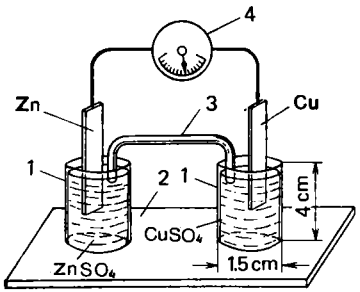


Fig. 37.
Voltaic cell:
1–beakers; *2*–base plate; *3*–salt bridge; *4*–galvanometer

and a copper plate into the copper sulphate solution. Connect the plates by an electric wire with galvanometer *4*. Observe deviation of the galvanometer pointer which indicates an electric current which arises due to the difference in the electrode potentials of zinc $\varphi_{Zn^{2+}/Zn}$ and copper $\varphi_{Cu^{2+}/Cu}$.

Recording the results. Draw an electric double layer at the interface of the metal and the solution of its salt at the zinc and copper electrodes. What is the qualitative difference?

Write down the equations for the chemical reactions occurring at the electrodes of the voltaic cell and the overall equation of the chemical reaction by which an electric current is generated in a given cell. In what direction do electrons move in the external circuit? Use Table 11 of the Appendix to find the standard electrode potentials for copper and zinc, and calculate the e.m.f. of the copper-zinc cell. What ions and in what direction move in the solution?

B. Concentration voltaic cell

Procedure. Fill two beakers (see Fig. 37) with solutions of zinc sulphate of different concentrations (the concentration of one solution is 1 *M* and of the other, 0.01 *M*). Connect the beakers by means of the salt bridge. Immerse zinc plates into the beakers and connect them by a wire with a galvanometer. Does the galvanometer pointer deviate?

Recording the results. Consult Table 11 of the Appendix and use the Nernst equation to calculate φ of each electrode. Write down the equations for the chemical processes occurring at the electrodes. In which direction will electrons move in the external circuit? Calculate the e.m.f. of the concentration cell.

2. Determining Electrode Potentials of Metals

It is impossible to measure directly the potential of a single electrode. The electrode potentials given in reference tables are relative values. They have been measured relative to a standard hydrogen electrode,

whose potential is assumed conventionally to be zero ($\varphi^{\circ}_{2H^+/H_2} = 0$). Other reference electrodes are more convenient in practical uses; their potentials are constant with respect to the standard hydrogen electrode. Calomel or silver chloride electrodes are frequently used. Their potentials relative to the standard hydrogen electrode are $\varphi^{\circ}_{AgCl/Ag} = +0.222$ V, $\varphi^{\circ}_{Hg_2Cl_2/Hg} = +0.268$ V with the KCl (1 *N* solution) filling.

In order to measure the e.m.f. of a voltaic cell made of a reference electrode and the electrode with unknown potential, potentiometer with two scales graduated in pH units and in millivolts is used.

Procedure. Determine the standard electrode potentials of copper $\varphi^{\circ}_{Cu^{2+}/Cu}$ and zinc $\varphi^{\circ}_{Zn^{2+}/Zn}$ using a silver chloride electrode.

Assemble a voltaic cell similar to that shown in Fig. 37. Beakers are covered with lids provided with two holes for electrode and a salt bridge. Place 1 *M* solution of $CuSO_4$ into one beaker to 2/3 its capacity and lower a copper plate into the solution. Fix the copper plate in the lid. Place KCl solution (1 *N*) into the other beaker and fix the silver chloride electrode in the lid so that the electrode is immersed in the solution. Connect the solutions via the salt bridge and connect electrodes by electric wires to the pH meter (millivoltmeter). After the pH-meter pointer stabilizes, note the e.m.f. of the copper-silver cell (in mV).

In order to determine the standard electrode potential of zinc, carry out a similar procedure to determine the e.m.f. of a voltaic cell made of zinc and silver chloride electrodes. To do so, substitute a beaker containing 1 *M* solution of $ZnSO_4$ for the copper half-cell, and immerse a zinc plate into it. Write down the readings of the millivoltmeter.

Recording the results. Calculate standard potentials φ° of the copper and zinc electrodes using the experimentally found e.m.f. of the cells and potential of silver chloride electrode $\varphi_{AgCl/Ag} = +0.222$ V. When calculating the potentials for copper and zinc, take into account that the e.m.f. of the former cell is equal to $\varphi_{Cu^{2+}/Cu} - \varphi_{AgCl/Ag}$, and the e.m.f. of the latter cell is equal to $\varphi_{AgCl/Ag} - \varphi_{Zn^{2+}/Zn}$.

Therefore, $\varphi_{Cu^{2+}/Cu} = \text{e.m.f.} + \varphi_{AgCl/Ag}$; $\varphi_{Zn^{2+}/Zn} = \varphi_{AgCl/Ag} - \text{e.m.f.}$ Compare the obtained data with those in Table 11 of Appendix.

3. Measuring e.m.f. of a Voltaic Cell with Inert Electrodes

In Daniell-Jacobi (copper-zinc) cells the metal electrodes are involved in the oxidation-reduction reaction of the cell. But most oxidation-reduction processes in solutions occur between simple and complicated ions. Inert electrodes are used to measure the e.m.f. of cells employing such oxidation-reduction reactions. Inert electrodes made

of platinum or graphite do not participate in chemical reactions but are only transmitters of electrons between reducing and oxidizing ions.

Procedure. Measure the e.m.f. of a voltaic cell in which the following oxidation-reduction reaction occurs:

$$Sn^{2+} + Fe^{3+} \rightleftarrows Sn^{4+} + Fe^{2+}$$

To do so, place a solution containing $SnCl_2$ and $SnCl_4$ salts (the concentration of each salt is 1 mol/l) into one beaker (see Fig. 37) and immerse a platinum wire into the solution. The following equilibrium is established at the platinum electrode: $Sn^{4+} + 2e^- \rightleftarrows Sn^{2+}$, which determines the electrode potential $\varphi_{Sn^{4+}/Sn^{2+}}$. Fill the other beaker with a solution of iron(III) and iron(II) salts (the concentration of each species of ions is 1 mol/l) and immerse a platinum wire into the solution. The equilibrium $Fe^{3+} + e^- \rightleftarrows Fe^{2+}$, which is established at the platinum electrode, determines the electrode potential $\varphi_{Fe^{3+}/Fe^{2+}}$. Interconnect the beakers through a salt bridge and connect the electrodes to the potentiometer. Record the e.m.f. of the cell in millivolts.

Recording the results. Using the data from Table 11 of Appendix, calculate the e.m.f. of the voltaic cell in question. Compare its e.m.f. with the tabulated data.

4. Direction of Oxidation-reduction Reactions

Procedure. Determine the direction of the oxidation-reduction reaction

$$Cr_2(SO_4)_3 + K_2SO_4 + I_2 + H_2O \rightleftarrows K_2Cr_2O_7 + KI + H_2SO_4$$

Place 2-3 drops of chromium(III) sulphate and of potassium sulphate solution into a test tube and add 1-2 drops of iodine water. Is chromium(III) oxidized with iodine? (Oxidation should be accompanied by decolourization of iodine.)

Place a few drops of potassium dichromate and sulphuric acid solution into another test tube and add 3-4 drops of potassium iodide. Why has the solution turned brown? In what direction (forward or reverse) does the oxidation-reduction reaction proceed?

Recording the results. Write down the equations for the half-reactions of the oxidation and reduction for the given oxidation-reduction reaction. Consider this reaction as a process occurring in a voltaic cell. Write down the corresponding electrode potentials (see Table 11 of the Appendix) and calculate the e.m.f. Note that the e.m.f. of this oxidation-reduction process is positive and that the oxidized form of the voltaic pair with a higher electrode potential

is the oxidant in this oxidation-reduction reaction, while the reduced form of the pair with a lower potential is the reductant.

Consider the values of electrode potentials, and decide if the following reaction can occur at STP

$$MnO_4^- + Br_2 + H^+ \rightarrow Mn^{2+} + BrO_3^- + H_2O$$

Explain your answer.

5. Formation of Voltaic Pairs in Chemical Processes

A. Interaction between zinc and sulphuric acid in the absence and presence of copper

Procedure. Place 5-6 drops of 2 *N* sulphuric acid into a test tube and add a grain of pure zinc (without impurities). Is hydrogen displaced from the acid? Using a copper wire, touch the zinc grain in the test tube. How does the intensity of hydrogen liberation change and on which metal is hydrogen liberated? Remove the copper wire and make sure that the hydrogen liberation intensity changes again. Indicate the direction of the electron transfer in the zinc-copper pair. Which metal will bear a negative charge and act as a cathode for the hydrogen ion in the solution?

Observe the same effect in the following experiment.

Place 5-6 drops of 2 *N* sulphuric acid into each of two test tubes. Add a drop of copper sulphate solution into one test tube, then add a grain of pure zinc into both test tubes. Observe the different intensity of hydrogen liberation. What is observed on the surface of zinc in the presence of copper sulphate? What role does copper salt play in the reaction of hydrogen displacement?

B. Corrosion of zinc-plated and tin-plated iron

Procedure. Half fill two test tubes with distilled water and add 2-3 drops of 2 *N* sulphuric acid and of potassium ferricyanide solution into both test tubes. Potassium ferricyanide is a specific reagent for Fe^{2+} ions (forming a blue compound with them). Stir the solutions using a glass rod.

Clean two lengths of an iron wire with emery paper. Use one wire to wind it round a grain of zinc and the other round a piece of tin. Drop both into the prepared solutions. Observe the blue colour in the solution containing the iron wire with tin. Explain the appearance of Fe^{2+} ions in the solution. The solution containing the iron-zinc pair does not change its colour. Why?

Recording the results. Describe the observed phenomena and answer the questions. Draw up a diagram of electron transfer during

corrosion of zinc- and tin-plated iron and indicate, in which case the iron corrodes under an intact coat if only part of this coating is damaged. Which metal will corrode first in the following pairs: aluminium-copper, copper-nickel, iron-nickel?

6. Preparing Lead Accumulator

Procedure. Fill a 50-70-ml wide-mouth bottle *1* (Fig. 38) with a 3.5 *M* solution of sulphuric acid to 2/3 its capacity. Close the bottle with stopper *2* in which two lead plates or lead foil strips *3* are fixed at a distance of 3-4 cm from each other. There is a vent *4* in the stopper through which gas outlet is ensured. How do the surfaces of the lead plates immersed in sulphuric acid change due to deposition of insoluble lead sulphate on them?

Place a sheet of filter paper *6* on a glass slide, wet the paper with sodium chloride solution (or any other salt of sodium or potassium) and apply 2-3 drops of phenolphthalein. Attach wires *5* to each plate and press their free ends to the wet filter paper at a distance from each other. Make sure that the accumulator is inactive.

Now charge the accumulator by connecting the wires to the terminals of a flash-light battery (4.5-5 V) for 4-5 minutes.

Disconnect the cell from the source of electricity and press the free ends of the wires to the wet paper again. The wire, round which a red spot is formed, is the negative pole of the working accumulator (cathode).

Recording the results. A dense layer of sparingly soluble lead sulphate is formed on the lead plates when they are immersed into sulphuric acid. This layer prevents further reaction of lead with the acid. How does the formation of this protective sulphate film on the lead surface show itself in this experiment?

As the accumulator is charged, Pb^{2+} ions (from $PbSO_4$) accept two electrons at the cathode of the external source of electricity and

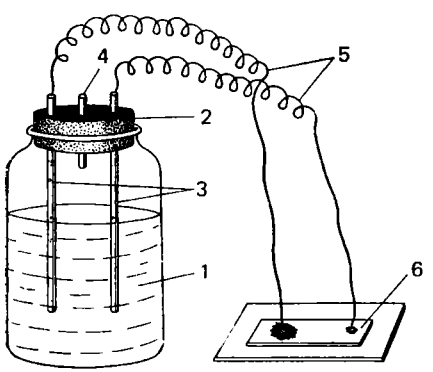


Fig. 38.
Lead accumulator:
1 – wide-mouth bottle;
2 – stopper; *3* – lead electrodes;
4 – vent; *5* – electric wires;
6 – filter paper

are reduced to metallic lead; at the anode these ions give off their two electrons and are oxidized to PbO_2. During charging of the accumulator, electric energy is converted into chemical. The processes thus occurring can be expressed by the ionic equations:

$PbSO_4 + 2e^- = Pb + SO_4^{2-}$ (at the cathode)

$PbSO_4 - 2e^- + 2H_2O = PbO_2 + 4H^+ + SO_4^{2-}$ (at the anode)

Summation of these two simultaneous processes gives the equation of the reaction occurring during charging of the accumulator:

$2PbSO_4 + 2H_2O = Pb + PbO_2 + 4H^+ + 2SO_4^{2-}$

The charged accumulator is a voltaic cell employing a spontaneous oxidation-reduction reaction:

$Pb + PbO_2 + 4H^+ + 2SO_4^{2-} = 2PbSO_4 + 2H_2O$

During the discharge of the accumulator, chemical energy is converted into electrical and the chemical reactions are "reversed": the lead electrode becomes the anode, while the PbO_2 electrode becomes the cathode. The electrode reactions are as follows:

$PbO_2 + 2e^- + 4H^+ + 2SO_4^{2-} = PbSO_4 + 2H_2O$ (at the cathode)

$Pb - 2e^- + SO_4^{2-} = PbSO_4$ (at the anode)

Explain the appearance of a red spot on the filter paper due to electrolysis of the aqueous solution of sodium chloride, for which the prepared accumulator is the source of current.

EXPERIMENT 21. ELECTROLYSIS OF AQUEOUS SOLUTIONS

Apparatus and reagents	
A set-up for electrolysis. Graphite rods. Flash-light battery. Copper wire. Electric drive. Phenolphthalein. Solutions: tin(II) chloride, 0.5 *N*;	potassium iodide, 0.1 *N*; sodium sulphate, 0.5 *N*; titanium(IV) sulphate, 0.5 *N*; neutral litmus; starch; nickel(II) sulphate, 0.5 *N*; sodium thiosulphate, 0.5 *N*; copper(II) sulphate, 0.5 *N*.

1. Electrolysis of Aqueous Solutions with Inert Electrodes

The experiments are carried out in an apparatus shown in Fig. 39. The electrolyzer is a U-tube *1* fixed in stand *3*. The electrodes *2* are graphite (pencil cores) or metal wires fixed in rubber stoppers. The stoppers should not tightly close the electrolyzer tube. A flash-light battery *4* can serve as a source of electric current. During the experiment, the electrolyzer should be filled to 1/2 its capacity. The electrodes should be washed thoroughly with distilled water before each experiment.

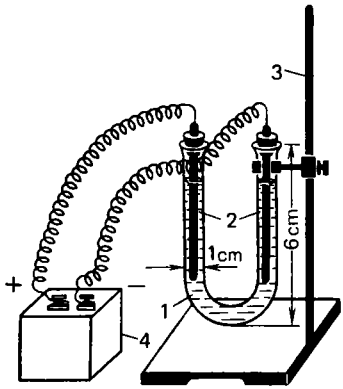


Fig. 39.
Set-up for electrolysis:
1 – U-tube; *2* – electrodes;
3 – ring stand;
4 – flash-light battery

A. Electrolysis of tin(II) chloride solution

Procedure. Half fill the electrolyzer with a tin(II) chloride solution. Immerse the graphite electrodes in the U-tube and connect them to the battery using copper wires. Observe deposition of lustrous crystals of tin on the cathode. Is tin oxidized or reduced at the cathode? Write down the equation for the cathode reaction. Prove that free chlorine is liberated at the anode. To do so, remove the anode from the electrolyzer after an electric current has been passed through the solution for 4-5 minutes; add 3-4 drops of potassium iodide and of starch solutions into the anode compartment, and observe the appearance of blue colour. Write down the equation for the anode reaction.

B. Electrolysis of potassium iodide solution

Procedure. Place potassium iodide solution into a conical test tube (to 3/4 of its capacity) and add 5-6 drops of phenolphthalein and of starch solution. Stir the mixture and pour it into the electrolyzer. Immerse graphite electrodes and connect them to a source of electric current.

Note the colour change of the solution in the vicinity of the cathode and the anode. Write down the equations for the anode and cathode reactions. Why did the colour of the solutions change in the anode and the cathode compartments? Is iodine oxidized or reduced at the anode?

Note: When the experiment is over, first wash the anode with sodium thiosulphate solution to remove iodine, and then rinse with distilled water.

C. Electrolysis of sodium sulphate solution

Procedure. Half fill a conical test tube with sodium sulphate solution and add 1/4 of test tube volume of neutral litmus. Stir the mixture and pour it into the electrolyzer. Pass electric current through the solution and observe the colour change in both arms of the U-tube.

Write down the equations for the anode and cathode reactions occurring during the electrolysis of sodium sulphate. What substances are liberated at the anode and at the cathode? Explain the colour change of litmus in the cathode and the anode compartments.

D. Electrolysis of titanium(IV) sulphate solution

Procedure. Fill the electrolyzer with a solution of titanium(IV) sulphate, immerse graphite electrodes and pass electric current. Observe the appearance of violet colour in one arm of the electrolyzer, which is due to the formation of Ti^{3+} ions.

At which electrode are Ti^{3+} ions formed? Write down the equation for the reaction of electrolytic reduction of titanium.

2. Electrolysis of Aqueous Solutions with Soluble Anodes

Procedure. Place a 0.5 *N* copper sulphate solution into an electrolyzer, immerse graphite electrodes into the solution and pass electric current for several minutes. Disconnect the electrodes from the source of electricity and observe a red deposit of copper on the cathode. Write down the equation for the cathode and anode reactions. What gas is liberated in small quantity at the anode?

Without disconnecting the electrolyzer from the source of electricity, change places of the electrodes in the electrolyzer so that the copper-coated cathode is now the anode. Pass electric current again. What occurs to the copper at the anode? What substance is deposited at the cathode? Write down the equations for the cathode and the anode reactions occurring during electrolysis of copper sulphate with a copper anode.

Carry out a similar experiment using a 0.5 *N* nickel(II) sulphate solution. What substance is liberated at the cathode? Write down the equation for the cathode reduction of nickel. What substance is oxidized at the anode during electrolysis of nickel sulphate with a carbon anode? with a nickel anode? Write down the equations for the corresponding anode reactions.

11 Complex Compounds

QUESTIONS AND PROBLEMS

1. Determine the oxidation state and the coordination number of the complexing agent in the following complex compounds and give their names:

(a) $K[AuBr_4]$
(b) $K_2[Cd(CN)_4]$
(c) $Ca[ZrF_6]$
(d) $Na_3[Ag(S_2O_3)_2]$
(e) $[Pt(NH_3)_2Cl_2]$
(f) $K[PtNH_3Cl_5]$
(g) $H[Co(H_2O)_2(CN)_4]$
(h) $[Pt(NH_3)_5Cl]Cl_3$
(i) $Na_2[FeNO(CN)_5]$
(j) $K[Cr(SO_4)_2]$

2. Determine the sign and magnitude of charge on the complex ions. Write down the formulas of complex compounds incorporating the following cations or anions:

(a) $[Bi^{+III}I_4]$
(b) $[Cr^{+III}(NH_3)_5Cl]$
(c) $[Cr^{+III}(H_2O)_4Cl_2]$
(d) $[Co^{+III}(NH_3)_2(NO_2)_4]$
(e) $[Pd^{+II}(NH_3)_2(CN)_2]$
(f) $[Fe^{+III}F_6]$
(g) $[Hg^{+II}(SCN)_4]$
(h) $[Zr^{+IV}(OH)_6]$
(i) $[Ag^{+I}(CN)_2]$
(j) $[Fe^{+III}(H_2O)_5Br]$

3. Write down the coordination formulas for the following complex compounds, substantiate the choice of the complexing agent, and give names to these compounds:

(a) $3NaF \cdot AlF_3$
(b) $SiF_4 \cdot BaF_2$
(c) $2Ca(CN)_2 \cdot Fe(CN)_2$
(d) $2Ba(OH)_2 \cdot Cu(OH)_2$
(e) $CoCl_3 \cdot 4NH_3 \cdot H_2O$
(f) $2KNO_3 \cdot HNO_3 \cdot Au(NO_3)_3$
(g) $2NH_4Br \cdot CuBr_2 \cdot 2NH_3$
(h) $3NaCl \cdot IrCl_3$
(i) $3KCN \cdot Fe(CN)_3$
(j) $Cd(OH)_2 \cdot 4NH_3$
(k) $KCl \cdot PtCl_4 \cdot NH_3$
(l) $KCN \cdot Co(CN)_3 \cdot 2H_2O$
(m) $NH_4CN \cdot Cr(CN)_3 \cdot 2H_2O$

4. Write down the coordination formulas for the following complex compounds and name them:

(a) $PtCl_4 \cdot 6NH_3$
(b) $PtCl_4 \cdot 5NH_3$
(c) $PtCl_4 \cdot 4NH_3$
(d) $PtCl_4 \cdot 3NH_3$
(e) $PtCl_4 \cdot 2NH_3$

5. The coordination number of cobalt(III) is six. Write down the coordination formulas for the following complex compounds:

(a) $Co(NO_2)_3 \cdot 6NH_3$
(b) $Co(NO_2)_3 \cdot KNO_2 \cdot 2NH_3$
(c) $Co(NO_2)_3 \cdot 3NH_3$
(d) $Co(NO_2)_3 \cdot 3KNO_2$

6. Write down the equations for dissociation of complex ions in the following compounds and also the instability constants for the complex ions:

(a) $K_3[Fe(CN)_6]$
(b) $[Co(H_2O)_2(NH_3)_4]Cl_3$
(c) $[Co(H_2O)(NH_3)_4Cl]Cl_2$
(d) $Cs[Ag(CN)_2]$
(e) $K[VF_6]$
(f) $Ba[BF_5]$
(g) $Na_2[MoF_6]$
(h) $K_2[Zr(OH)_6]$

7. What independent molecules are contained in the following complex compounds:

(a) $Na_2[Ni(CN)_4]$
(b) $[Cr(NH_3)_3H_2OCl_2]Cl$
(c) $Cs[AuCl_4]$
(d) $Na_2[Pt(OH)_6]$

(e) $H[Co(H_2O)_2(CN)_4]$ (h) $[Cr(NH_3)_3(H_2O)_3]Cl_3$
(f) $K_2[PdBr_4]$ (i) $(NH_4)_2[Fe(SO_4)_2]$
(g) $Ba_2[Co(OH)_6]$ (j) $[Cr(NH_3)_4C_2O_4]Cl$

8. Silver nitrate precipitates all chlorine from a solution of the complex salt $CoCl_3 \cdot 6NH_3$, while from the solution of $CoCl_3 \cdot 5NH_3$ it precipitates only 2/3 of chlorine. Write down the coordination formulas for these salts and equations for their dissociation.
9. Write down the molecular and ionic equations for the exchange reactions between the following compounds:

(a) $CdSO_4 \cdot 4NH_3 + BaCl_2 =$
(b) $PtCl_4 \cdot 2NH_3 \cdot H_2O + AgNO_3 =$
(c) $Fe(CN)_2 \cdot 4KCN + FeCl_3 =$

10. Which base is stronger, $[Cu(NH_3)_4](OH)_2$ or $Cu(OH)_2$? Explain your answer.
11. Which acid is stronger, HCN or $H[Ag(CN)_2]$? Explain.
12. The degree of hydrolysis of which salt is higher:
(a) KCN or $K[Ag(CN)_2]$; (b) $ZnCl_2$ or $[Zn(NH_3)_4]Cl_2$? Explain your answer.
13. Copper sulphate solution reacts with sodium hydroxide and ammonium sulphide solution to give precipitates. Tetramminecopper sulphate forms a precipitate only with ammonium sulphide. Explain these facts. Consult the Table of Solubility Products and that of K_{Inst} (Tables 8 and 12 of Appendix).
14. Which complex is more stable in the following pairs:
(a) $[Zn(NH_3)_4]^{2+}$ or $[Cd(NH_3)_4]^{2+}$
(b) $[Co(NH_3)_4]^{2+}$ or $[Co(NH_3)_6]^{3+}$
Explain your answer. Do their instability constants (see Table 12 of Appendix) agree with your conclusions?
15. Which complexing agent gives more stable complexes:
(a) Pt^{4+} or Pt^{2+} (c) Mg^{2+} or Ni^{2+}
(b) Ca^{2+} or Zn^{2+} (d) Zn^{2+} or Cd^{2+}
Explain your answer.
16. Draw up structural formulas for *cis*- and *trans*-isomers of tetrachlorodiammineplatinum(IV).
17. There exist two complex compounds of cobalt of the same composition: $CoClSO_4 \cdot 5H_2O$. The solution of one salt gives a precipitate in reaction with barium chloride solution, and does not react with silver nitrate solution. A solution of the other salt forms a precipitate with silver nitrate but does not react with barium chloride. Write down the coordination formulas for both compounds.
18. What complex compounds are known as chelates? Give two examples.
19. Determine a possible type of hybridization of electron orbitals of a complexing agent in the following complexes (take into consideration their magnetic properties):
(a) $[Co(NH_3)_6]^{3+}$ (paramagnetic);
(b) $[Co(NH_3)_6]^{2+}$ (diamagnetic).
20. What are the types of hybridization of electron orbitals of a complexing agent and the spatial configuration of the ions of $[Zn(NH_3)_4]^{2+}$ and $[Ni(CN)_4]^{2-}$ complex particles?

Examples of Multiple-choice Questions

1. What separate molecules form $Na_2[FeNO(CN)_5]$?

(1) $NaNO_2 \cdot Fe(CN)_6$ (2) $NaCN \cdot NO \cdot Fe(CN)_3$
(3) $Fe(CN)_2 \cdot NaCN \cdot NO$ (4) $Na_2O \cdot Fe(CN)_5 \cdot NO$
(5) $2NaCN \cdot Fe(CN)_3 \cdot NO$

2. What is the oxidation state of a complexing agent in $[Pt(NH_3)_5Br](NO_3)_3$?
(1) +I; (2) +II; (3) +III; (4) +IV; (5) +V.

3. What coordination formula is valid for the compound $NaBr \cdot CuBr_2 \cdot H_2O$?

(1) $Cu[NaBr_3 \cdot H_2O]$ (2) $Na[CuBr_3]H_2O$
(3) $Na[CuH_2O \cdot Br_3]$ (4) $CuBr[NaBr_2H_2O]$
(5) $Na[CuBr_2 \cdot H_2O]Br$

4. In which of the following compounds is the charge of the complexing agent the lowermost?
(1) $K[Cr(SO_4)_2]$; (2) $K_3[Fe(CN)_6]$; (3) $K[VF_6]$; (4) $[Pt(NH_3)_2Cl_2]$; (5) $H[AuCl_4]$.
5. What is the spatial configuration of the complexes formed during d^2sp^3-hybridization of atomic orbitals?
(1) plane square; (2) tetrahedron; (3) trigonal bipyramid; (4) octahedron; (5) linear.

EXPERIMENT 22. COMPLEX COMPOUNDS

Apparatus and reagents

Water bath.
Dropping pipette. Cobalt chloride hexahydrate. Chromium chloride hexahydrate. Mohr's salt.
Litmus paper, red.
Amyl alcohol. Tin granules.
Zinc granules. Solutions: hydrochloric acid, 2 *N*; sulphuric acid, 2 *N*; oxalic acid, 1 *N*; citric acid, 1 *N*; sodium hydroxide, 2 *N*; ammonia solution, 25%;
potassium iodide, 0.5 *N*; bismuth nitrate, 0.5 *N*; mercury(II) nitrate, 0.5 *N*; silver nitrate, 0.1 *N*; nickel sulphate, 0.5 *N*; copper sulphate, 1 *N* and 0.5 *N*; cadmium sulphate, 0.5 *N*;
chromium chloride, 0.5 *N*; aluminium sulphate, 0.5 *N*; zinc sulphate, 0.5 *N*; iron(III) chloride, 0.5 *N*; ammonium thiocyanate, saturated; potassium ferrocyanide, 0.5 *N*; potassium ferricyanide, 0.5 *N*; potassium permanganate, 0.5 *N*;
barium chloride, 0.5 *N*;
ammonium oxalate, 0.5 *N*;
ammonium sulphide.

1. Tetramminecopper(II) Sulphate. Its Properties*

Procedure. Place 10 drops of 1 *N* copper sulphate solution into each of two test tubes and add 2 drops of barium chloride to one of them. Which ion is responsible for the precipitate? Add a grain of tin into the other test tube and observe the formation of a red copper coat on its surface.

Obtain a complex compound of copper. To do this, place 15-16 drops of a copper sulphate solution into a test tube and add, drop by drop, 25% ammonia solution. Basic copper sulphate first precipitates and then dissolves. Observe the colour change during formation of the complex tetramminecopper(II) sulphate. Divide the obtained solution into two portions and carry out the same two reactions that were carried out with copper sulphate solution. Does any substance precipitate as barium chloride is added? Does copper precipitate on the tin grain?

* Some students can be recommended to carry out Experiment 24 "Synthesis of Tetramminecopper(II) Sulphate".

Recording the results. Write down the equations for all reactions. Do copper sulphate and the complex salt of copper react similarly with added reagents? It is known from the molar electric conductivity of the solution of the complex compound that it dissociates into two ions. Now write down its coordination formula and the equation for its electrolytic dissociation.

2. Anion Complexes

A. Potassium tetraiodobismuthate

Procedure. Place 3-4 drops of bismuth nitrate into a test tube and add, drop by drop, potassium iodide solution until a dark brown bismuth iodide precipitates. Dissolve this precipitate in excess potassium iodide solution.

Recording the results. What is the colour of the obtained solution? Can this colour be due to the presence of K^+, I^- or Bi^{3+} ions? Which of these ions can be a complexing agent? With which ligands can it form a complex ion in this solution? Explain your answer.

The empirical formula of the obtained compound is $KI \cdot BiI_3$. Write down its coordination formula. Write down the equations for the reactions of formation of bismuth iodide, and for the interaction between bismuth iodide and excess potassium iodide. Write down the equation for electrolytic dissociation of the obtained complex compound.

B. Potassium tetraiodomercurate

Procedure. Place 2-3 drops of mercury(II) nitrate solution into each of two test tubes. Keep one of them as a reference and add a solution of potassium iodide to the other to complete dissolution of the orange precipitate (mercury(II) iodide) which first falls out. Test both solutions for the presence of Hg^{2+} ions, by adding 2 drops of sodium hydroxide to each test tube.

Recording the results. In which test tube does yellow mercury(II) oxide precipitate? Why no substance precipitates from the solution in the second test tube as the alkali is added?

Write down the equations for the reactions of formation of mercury(II) iodide and for the reaction between mercury iodide and excess potassium iodide (the coordination number of the Hg^{2+} ion is 4).

Write down the equation for electrolytic dissociation of mercury(II) nitrate and of the obtained complex salt, potassium tetraiodomercurate $K_2[HgI_4]$.

C. Hydroxy complexes

Procedure. Place solutions of salts of zinc, chromium(III) and aluminium into each of three test tubes and add, drop by drop, alkali solution into each. Observe precipitation of substances in the test tubes which are then dissolved in excess alkali.

Recording the results. Write down the equations for the reactions, taking into account that soluble hydroxy complexes containing $[Zn(OH)_4]^{2-}$, $[Cr(OH)_6]^{3-}$ and $[Al(OH)_6]^{3-}$ ions are formed. Since the hydroxides of zinc, chromium and aluminium dissolve also in acids, indicate what types they are.

3. Cation Complexes

A. Complex nickel base

Procedure. Precipitate nickel(II) hydroxide by adding to 3-4 drops of nickel sulphate solution the same volume of sodium hydroxide solution. Remove the liquid phase using a strip of filter paper.

Add 5-6 drops of 25% ammonia solution to the precipitate and observe the reaction. Compare the colour of Ni^{2+} ions in nickel sulphate solution to the colour of the obtained solution.

Which ion in the solution accounts for the colour?

Recording the results. Write down the equations for the following reactions: formation of nickel(II) hydroxide, the reaction between nickel hydroxide and ammonia, and electrolytic dissociation of the complex base (coordination number of nickel is 6). Which base is stronger, the simple or complex one? Explain your answer.

B. Complex base of cadmium

Procedure. Precipitate cadmium hydroxide in a test tube by mixing equal volumes of sodium hydroxide and cadmium salt solutions. Act with 25% ammonia solution on the obtained hydroxide of cadmium to dissolve the precipitate.

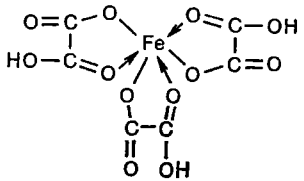
Recording the results. Write down the equations for the reaction by which cadmium tetrammine hydroxide is obtained and for its electrolytic dissociation. Which base is a stronger electrolyte, cadmium hydroxide or its complex base? Explain your answer.

4. Chelate Compounds

Procedure. Place 3 drops of iron(III) chloride solution into each of three test tubes. Keep one as a reference, and add 3 drops of alkali to the other two test tubes: precipitates fall out. Add 12-15 drops of a 2 *N* oxalic acid COOH—COOH into one test tube and the same

amount of a 2 *N* citric acid $CH_2(COOH)—C(OH)COOH$ to the other. Add 1-2 drops of a 0.01 *N* potassium (or ammonium) thiocyanate solution to all the three test tubes. The thiocyanate reacts with Fe^{3+} ions to give a bright coloured ferric thiocyanate $Fe(SCN)_3$. Does the colour appear in all test tubes?

Recording the results. Iron(III) hydroxide dissolves in oxalic and citric acids to form chelate compounds, in which the carboxyl groups of the acids are attached to the complexing agent. The structural formula of the oxalic complex is:



Is the oxalic acid residue a mono- or polydentate ligand? Draw a similar formula for the citrate complex. Note the great stability of the chelate compounds.

5. Complex Compounds in Exchange Reactions

A. Reaction of ammonium tetrathiocyanomercurate with cobalt salt

Procedure. Prepare a solution of ammonium tetrathiocyanomercurate. To that end place 3-4 drops of mercury(II) nitrate solution into a test tube and add a saturated solution of ammonium thiocyanate to complete dissolution of the mercury thiocyanate that first precipitates.

Place 4-5 drops of cobalt nitrate solution into another test tube and add an equal volume of the prepared ammonium tetrathiocyanomercurate solution. To accelerate precipitation, shake the test tube slightly. Note the colour of the precipitated cobalt tetrathiocyanomercurate.

Recording the results. Write down the equations for

(a) formation of mercury thiocyanate;

(b) reaction of mercury thiocyanate with excess ammonium thiocyanate if it is known that a complex salt is thus obtained in which the coordination number of mercury is 4;

(c) the ionic and molecular equations for the reaction of formation of cobalt tetrathiocyanomercurate.

B. Reaction of potassium ferrocyanide with copper sulphate

Procedure. Place 4-5 drops of copper sulphate solution into a test tube and add the same volume of the solution of the complex salt

$K_4[Fe(CN)_6]$. Note the colour of the precipitated copper hexacyanoferrate. Write down the ionic and molecular equations for the reaction.

6. Complex Compounds in Oxidation-reduction Reactions

A. Reduction of silver from its complex compound

Procedure. Place 5-6 drops of silver nitrate solution into a test tube and add sodium chloride solution. Dissolve the obtained precipitate in a 25% ammonia solution. Drop a grain of zinc into the solution and observe the reaction.

Recording the results. Write down the equations for the reactions by which silver chloride is precipitated, by which the precipitate is dissolved in ammonia solution with formation of a silver complex, and the reaction between the obtained complex compound and zinc. What ion is the oxidant in the latter reaction? Write down the equation for electrolytic dissociation of the complex ion and the ionic equation for the oxidation-reduction reaction.

B. Reduction of potassium ferricyanide

Procedure. Place 8-10 drops of 0.1 *N* potassium iodide solution into a test tube, add 6-8 drops of 2 *N* hydrochloric acid solution and 5-6 drops of benzene. Note that benzene remains colourless. Add a microspatula of crystals of the complex salt $K_3[Fe(CN)_6]$ and stir the solution using a glass rod. The change of benzene colour indicates liberation of free iodine.

Recording the results. Write down the equation for the reaction between potassium ferricyanide and potassium iodide taking into account that $K_3[Fe(CN)_6]$ converts into $K_4[Fe(CN)_6]$. Omit the acid from the reaction equation. Indicate the oxidant and the reductant in the reaction.

C. Oxidation of potassium ferrocyanide

Procedure. Place 4-5 drops of potassium permanganate solution into a test tube, acidify with 2 *N* sulphuric acid and add, drop by drop, potassium ferrocyanide until the solution becomes colourless.

Recording the results. Write down the reaction equation remembering that the ferrous complex is converted into the ferric complex by this reaction (the coordination number remains the same), while potassium permanganate is reduced in an acidic medium to manganese(II) sulphate.

7. Stability of Complex Ions. Decomposition of Complexes

A. Decomposition of complex by dilution

Procedure. Place 2 drops of silver nitrate solution into a test tube and add 0.1 *N* potassium iodide solution, drop by drop, with shaking the test tube after adding each next drop.

Why does silver iodide, which first precipitates, dissolve? Add 4-5 drops of water to the obtained solution and observe the reaction.

Recording the results. Describe your observations. Write down the equations for the reactions of formation of silver iodide, its conversion into a complex compound, and dissociation of the complex ion. Write down the expression for the instability constant. How does dilution influence dissociation of the complex ion?

B. Comparative stability of the cobalt thiocyanate complex in water and alcohol

Procedure. Obtain ammonium tetrathiocyanocobaltate(II) $(NH_4)_2 \times [Co(SCN)_4]$ in a test tube by reacting 2-3 drops of a saturated cobalt(II) chloride solution with 8-10 drops of a saturated ammonium thiocyanate solution. Note the lilac colour of the complex compound. Divide the solution into two test tubes. Add amyl alcohol to one test tube and 10 drops of water to another. Observe the colour change in the test tubes.

Recording the results. Write down the equations for the reactions of formation of the complex compound, its dissociation, and the dissociation of the complex ion. Is dissociation of the complex ion more complete in water or alcohol? Explain your answer.

C. Decomposition of complex during precipitation of complexing agent

Procedure. Place copper sulphate solution into each of two test tubes and add ammonium oxalate solution into one and ammonium sulphide into another test tube. Write down the equations for the reactions and note the colour of the precipitates. Prepare a complex compound of copper in two other test tubes by adding ammonia solution to 4-5 drops of 1 *N* solution of $CuSO_4$ contained in each test tube to dissolve the basic copper salt which first precipitates. Note the colour of the obtained complex compound. Write down the equation for the reaction between copper sulphate and ammonia solutions, taking into consideration that the coordination number of copper is 4.

Test the effect of ammonium oxalate and ammonium sulphide on the obtained solution of the complex copper salt. Which of the two reagents causes precipitation? Which ions in the complex salt solu-

tion account for the precipitate? Add 6-7 more drops of the same precipitant to the test tube with the precipitate. To accelerate coagulation place the test tube into a boiling water bath. Does the colour of the copper complex persist in the solution?

Recording the results. Describe your observations. Answer the questions. Write down the equations for the reactions and for the electrolytic dissociation of the complex copper salt and its complex ion. How does the addition of $(NH_4)_2S$ affect the dissociation of the complex ion? Consult Table 8 of Appendix to compare solubility products of the corresponding copper salts and explain why one of them does not precipitate from the complex compound.

8. Double Salts

Procedure. Prepare a solution of the double (Mohr's) salt $(NH_4)_2SO_4 \cdot FeSO_4 \cdot 6H_2O$ in three separate test tubes by dissolving a microspatula of the salt in 6-8 drops of water. Add 5-6 drops of ammonium sulphide solution to one test tube and the same volume of barium chloride to another test tube. The black precipitate is iron(II) sulphide. Note the colour of the precipitates and write down the ionic equations for the precipitation reactions. Which ions in the solution of the double salt participate in this precipitation?

Add 7-8 drops of 2 *N* sodium hydroxide solution to the third test tube, fix it in the stand, and immerse into a water bath heated almost to boiling. Hold a moist red litmus paper above the mouth of the test tube. Identify the evolving gas by the odour and the colour of litmus paper. Write down the ionic equation for the reaction in which this gas is evolved. Which ions of the double salt are involved in this reaction? Write down the equation for the electrolytic dissociation of Mohr's salt.

Act with ammonium sulphide solution on the solution of $K_4[Fe(CN)_6]$ to check the presence of Fe^{2+} ions in the solution. Does black FeS precipitate? Explain.

Recording the results. Describe your observations. Answer the questions. Write down the equations for the corresponding reactions. Write down the equations for electrolytic dissociation of $K_4[Fe(CN)_6]$. How does the electrolytic dissociation of the double salt differ from dissociation of a salt containing a stable complex ion?

9. Isomerism of Aqua Complexes of Chromium(III)

Chromium chloride $CrCl_3 \cdot 6H_2O$ forms isomers of different colours:

$[Cr(H_2O)_6]Cl_3$ — blue-violet

$[Cr(H_2O)_5Cl]Cl_2 \cdot H_2O$ — dark-green

$[Cr(H_2O)_3Cl_3] \cdot 3H_2O$ — pale-green

All these three isomers are at equilibrium in the solution. This equilibrium depends on various factors; for example it strongly depends on temperature.

Procedure. Place several crystals of chromium chloride $CrCl_3 \times \times 6H_2O$ into each of two test tubes and add 10 drops of water to both. Save one as a reference, and heat the other on a boiling microbath. Observe the colour change.

Which isomer of the aqua complex of chromium(III) is more stable at room temperature? At high temperature? Give systemic names for the three isomers.

EXPERIMENT 23. SYNTHESIS OF COMPLEX SALT OF POTASSIUM TETRAIODOMERCURATE(II) $K_2[HgI_4]$ AND STUDY OF ITS PROPERTIES

Apparatus and reagents

Beaker, 100-ml.
Cylinder, 10-ml. Porcelain dish.
Desiccator with sulphuric acid.
Büchner funnel. Microscope.
Potassium iodide.
Mercury(II) nitrate. Solutions: chlorine water, tin(II) chloride, 0.5 *N*; potassium chloride, 0.5 *N*; reagent for potassium ion (dissolve 2 g $NaNO_2$, 0.9 g $Cu(C_2H_3O_2)_2$, 1.7 g $Pb(C_2H_3O_2)_2$ and 0.3 ml of 30% acetic acid in 15 ml of water); starch.

Procedure. Calculate the necessary amount of 0.5 *N* solutions of potassium iodide and mercury(II) nitrate to obtain 5 g of mercury(II) iodide precipitate by an exchange reaction. Prepare this salt, allow mercury iodide to settle, filter it and wash with water.

Dissolve 10 g of potassium iodide in 10 ml of hot water in a 100-ml beaker and cool the solution. Then, dissolve the freshly prepared mercury iodide in this solution to saturation. Transfer the obtained solution into a porcelain dish and place the dish into a desiccator for crystallization. Using a glass rod, break the crust on the surface from time to time in order to facilitate evaporation. Filter the formed crystalline mass on a Büchner funnel and dry in a drying cabinet at 60-70°C.

The prepared orange-red crystals are the crystal hydrate of potassium tetraiodomercurate(II) $K_2[HgI_4] \cdot 2H_2O$. Write down the reaction equations.

Properties of the complex salt $K_2[HgI_4]$.

1. Determine the presence of the potassium ions in the solution of KCl and in the obtained complex salt by a microcrystalloscopic reaction with preparation of crystals of $K_2Pb[Cu(NO_2)_6]$. This salt precipitates in the form of black cubes visible under a microscope.

In order to prepare this salt, place a drop of $Na_2Pb[Cu(NO_2)_6]$ solution on a glass slide and, using a glass rod, add a grain of potassium iodide. Observe the formation of crystals under a microscope. Carry out the same reaction with the obtained complex compound. Are the crystals obtained in both reactions similar? Do the potassium ions belong to the inner or outer sphere of the complex compound?

2. Prove that the mercury and iodide ions are a part of the complex anion and that they cannot be detected by qualitative tests that are used for the analysis of compounds of these elements of the first order.

Place a small amount of the obtained compound into one test tube and potassium iodide into another. Dissolve the substances in a small amount of water. Add small volumes of chlorine water and 2-3 drops of starch solution to both test tubes. Observe the reactions.

3. Study the properties of mercury. To do so, dissolve a small amount of the obtained salt in a 0.5 *N* potassium iodide solution with heating. Place mercury(II) nitrate solution into another test tube. Add several drops of tin(II) chloride to both. Mercury(II) nitrate is reduced with tin(II) chloride according to the equation:

$$2Hg(NO_3)_2 + 2SnCl_2 = 2Hg + SnCl_4 + Sn(NO_3)_4$$

Mercury precipitates as a grey substance.

Explain the different behaviour of the two salts. Decide if the mercury and iodide ions belong to the inner or outer sphere of the complex compound.

Recording the results. Write down the equation for the reaction by which the complex compound is prepared and its dissociation. Write down the expression for the instability constant, and also equations for all reactions that were used to study the properties of the complex compound.

EXPERIMENT 24. SYNTHESIS OF TETRAMMINECOPPER(II) SULPHATE $[Cu(NH_3)_4]SO_4$ AND ITS PROPERTIES

Apparatus and reagents

Chemical balance.
Büchner funnel. Porcelain mortar.
Water-jet pump. Beaker, 100-ml.
Graduated cylinder, 100-ml.
Copper(II) sulphate pentahydrate.
Ethyl alcohol. Solutions: ammonia, 25% solution; barium chloride, 2 *N*; ammonium oxalate, 0.5 *N*; hydrogen sulphide solution.

Procedure. Weigh out 5 g of copper sulphate pentahydrate on a chemical balance, place it into a beaker. Calculate the amount of a 25% ammonia solution, necessary to prepare a complex com-

pound. In order to increase the yield of product, double the calculated quantity, since the solubility of the complex compound decreases in ammonia solution. Measure out the needed volume of the solution by a graduated cylinder and dissolve the pentahydrate in this ammonia solution in the beaker. Using a glass rod stir the mixture to complete dissolution. Add 10 ml of ethyl alcohol (the solubility of the complex compound in alcohol is lower than in water) and allow the solution to stand for 20-25 minutes for crystallization. Separate the precipitated crystals on a Büchner funnel and switch off the pump. Wash the precipitate on the filter two times with a mixture of equal volumes of alcohol and a 25% solution of ammonia solution. Place the alcohol-ammonia mixture into the funnel, allow the precipitate to get soaked with the mixture and start the pump again. If the pump is not switched off, the alcohol will rapidly soak through the precipitate and washing will thus be incomplete.

Weigh a weighing bottle on a chemical balance, transfer the crystals from the filter into the weighing bottle and place it into a drying cabinet. Dry at a temperature of 50-60°C for 20 minutes. Cool the weighing bottle and weigh it again. Calculate the yield of the complex compound with reference to the copper(II) sulphate pentahydrate.

Study the properties of $[Cu(NH_3)_4]SO_4$. Place a few crystals of the prepared salt into each of four test tubes and dissolve in small amounts of water. Detect the sulphate ion in one test tube by adding the appropriate reagent. Test the prepared complex ion for stability. To that end place an iron nail into the second test tube. Does copper precipitate on the iron? Add ammonium oxalate to the solution in the third test tube. Does copper oxalate precipitate? Add ammonium sulphide solution to the solution in the fourth test tube and observe the reaction. Place a few crystals of the salt into a dry test tube and heat slightly. Bring a moist ud litmus paper to the test tube mouth and observe if any colour change occurs.

Recording the results. Write down the equations for the reaction in which the complex compound is prepared and dissociated, and all reactions used to study its properties.

Which coordination sphere (inner or outer) of the complex compound contains copper ion? Explain the effect of ammonium oxalate and ammonium sulphide on the complex compound. To that end write down the equation for dissociation of the complex ion. Consult Tables 12 and 8 of Appendix to find its instability constant and the solubility products of the corresponding copper salts.

12 Elements of Subgroup VIIA

QUESTIONS AND PROBLEMS

1. Write down the electron structures for the halogen atoms in their ground and excited states. Why can chlorine, bromine, and iodine have oxidation states $-I$, $+VII$, $+V$, $+III$ and $+I$, while fluorine has only one oxidation state of $-I$?
2. Why are the halogen molecules diatomic?
3. Why is the F_2 molecule formed by only a covalent bond, while the Cl_2 molecule is formed by dative bonds? How do the bond energy and the strength of these molecules differ? Indicate the dative bond in the molecule of Cl_2.
4. How does the strength of bond between the atoms vary in the series Cl_2, Br_2 and I_2? Explain these variations. How do the stability of these molecules and the enthalpies of their dissociation change?
5. How do the energy of ionization and the electron affinity change in the series Cl, Br, I, At? Explain these variations.
6. In which oxidation state can the halogens have (a) only oxidizing properties, (b) only reducing properties, (c) oxidizing and reducing properties? Write down the corresponding electron structures for chlorine and iodine.
7. In which oxidation state can iodine have both oxidizing and reducing properties? Write down the formulas for the corresponding compounds.
8. What is the difference between the methods by which molecular halogens are prepared from the compounds containing the Hal^- and those containing $HalO_3^-$ ions? Write down two equations for the corresponding reactions for preparing chlorine.
9. Write down the equation for chemical equilibrium of chlorine water. What reagents should be used to prove the presence of (a) molecular chlorine, and (b) chloride ion in chlorine water? In what direction will the equilibrium be shifted if alkali is added?
10. Write down the equation for the reaction occurring during fluorine dissolution in water. Can "fluorine water" be prepared in the same way as chlorine water?
11. Write down the equations for the reactions by which hydrogen chloride is prepared by three different methods. Which of these reactions cannot be used to prepare hydrogen bromide and hydrogen iodide? Explain your answer. Write down the equations for the corresponding reactions.
12. How does the strength of chemical bonds change in the series HF, HCl, HBr, HI? How can these changes be explained?
13. Which of the hydrogen halides is the strongest and which is the weakest reductant? Using the table of electrode potentials, indicate which of the oxidants can oxidize (a) KI without oxidizing KBr, and (b) KBr without oxidizing KCl? Write down the equations for the corresponding reactions.
14. Which halogens can displace Br_2 from a solution of (a) KBr, and (b) $KBrO_3$? Write down the equations for the corresponding reactions and indicate the oxidant and the reductant in each particular reaction.
15. Which orbitals of the chlorine and iodine atoms are involved in the formation of bonds in the molecules of Cl_2O_7 and I_2O_5?
16. What type of chemical bond dominates in the molecules of hydrogen halides, halides of the alkali metals, and the halogen oxides?
17. Write down the formulas of chloride oxides in which chlorine is in the oxidation states of I, III, V and VII. Write down the formulas for the corresponding acids. Name these acids and indicate the sequence in which their electrolytic strength, stability and oxidizing properties change.

18. With which metals can hydrochloric acid react? Is the concentration of the acid important for the character of its reaction with metals? Explain your answer.
19. Complete the following equations and put proper coefficients:

(a) $I_2 + Cl_2 + H_2O = HIO_3 + \ldots$
(b) $K_2Cr_2O_7 + KI + H_2SO_4 = I_2 + Cr_2(SO_4)_3 + \ldots$
(c) $KClO_3 + MnO_2 + KOH = K_2MnO_4 + KCl + \ldots$
(d) $KCl + HNO_3 = NO + \ldots$
(e) $KIO_3 + KI + H_2SO_4 = I_2 + \ldots$
(f) $CaClO_2 + H_2O_2 = CaCl_2 + \ldots$
(g) $Ca(OH)_2 + Cl_2 =$
(h) $KClO_3 = KClO_4 + KCl$

20. Put appropriate coefficients and write down these equations in the molecular form:

(a) $IO_3^- + SO_3^{2-} + H^+ = I_2 + SO_4^{2-} + H_2O$
(b) $Br^- + MnO_4^- + H^+ = Br_2 + Mn^{2+} + H_2O$
(c) $ClO^- + MnO_4^{2-} + H_2O = Cl^- + MnO_4^- + OH^-$

Examples of Multiple-choice Questions

1. In which of the following reactions is bromine liberated?

(1) $KBr + I_2 \rightarrow$ (2) $KBr + KBrO_3 + H_2O \rightarrow$
(3) $KBrO_3 + I_2 \rightarrow$ (4) $KBrO_3 + Cl_2 \rightarrow$
(5) $KBr + H_2SO_3 \rightarrow$

2. What substances are obtained in the reaction between fluorine and water?
(1) HF + HFO; (2) $H_2 + F_2O$; (3) $H_2F_2 + O_2$; (4) H_2FO; (5) $H_2F_2O_2$.
3. Which of the following reactions can be used to obtain iodine?

(1) $KIO_3 + Cl_2 \rightarrow$ (2) $KIO_3 + KI + H_2O \rightarrow$
(3) $KIO_3 + Br_2 \rightarrow$ (4) $KI + Br_2 \rightarrow$
(5) $KI + SO_2 + H_2O \rightarrow$

4. In which of the following cases will chlorine be oxidized?
(1) $2Cl^- \rightarrow Cl_2$; (2) $2ClO^- \rightarrow Cl_2$; (3) $ClO_3^- \rightarrow ClO^-$; (4) $Cl_2 \rightarrow 2Cl^-$;
(5) $Cl_2 \rightarrow 2ClO_3^-$.
5. By what reagent can AgI and AgCl be separated in their mixture?
(1) H_2SO_4; (2) HNO_3; (3) NH_3 solution; (4) KBr; (5) KOH.

EXPERIMENT 25. THE HALOGENS

Apparatus and reagents

Apparatus for preparing hydrogen chloride (see Fig. 40). Glass rods. Asbestos-centred gauze. Crystallizer or porcelain dish. Beaker, 100-ml. Electric stove. Manganese dioxide. Sodium chloride. Sodium bromide. Potassium iodide. Potassium dichromate. Mohr's salt. Potassium perchlorate. Potassium permanganate. Potassium chlorate. Magnesium powder. Aluminium powder. Zinc powder. Indicators: litmus paper, litmus blue. Organic solvent. Solutions: chlorine water; bromine water; iodine water; hydrogen sulphide solution; sodium chloride, 0.5 *N*; sodium bromide, 0.5 *N*; potassium iodide, 0.1 *N*; silver nitrate, 0.1 *N*; iron(III) chloride, 0.5 *N*;

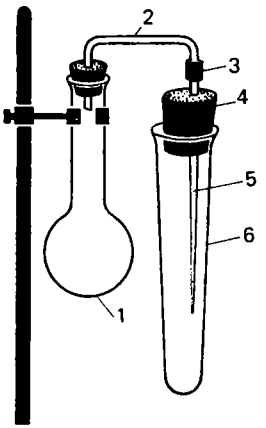


Fig. 40.
Apparatus for preparing hydrogen chloride:
1 – microflask;
2 – gas-discharge tube;
3 – rubber tubing; *4* – stopper;
5 – capillary tube; *6* – test tube

potassium chlorate, saturated; potassium perchlorate, 0.5 *N*; potassium dichromate, 0.5 *N*; potassium permanganate, 0.5 *N*; sodium thiosulphate, 0.5 *N*; sodium hydroxide, 2 *N*; hydrochloric acid (density 1.19 g/cm³; sulphuric acid (density 1.84 g/cm³; 70% solution); phosphoric acid, concentrated.

1. Preparing Halogens by Oxidizing the Halides

A. Preparing chlorine

Procedure. Place 2-3 crystals of $KMnO_4$ into one test tube and the same amount of $K_2Cr_2O_7$ into another test tube. Add 2-3 drops of concentrated hydrochloric acid (density 1.19 g/cm³) into each test tube. Heat slightly the test tube containing $K_2Cr_2O_7$. Observe liberation of chlorine.

Recording the results. Note the colour of chlorine. Write down the equations for the reactions, taking into account that potassium dichromate converts into chromium(III) chloride, while potassium permanganate into manganese(II) chloride. Indicate the oxidant and the reductant.

B. Preparing bromine and iodine

Procedure. Place 2-3 crystals of potassium (sodium) bromide and 1-2 microspatulas of manganese dioxide into one test tube and the same amount of a mixture of potassium iodide and manganese dioxide into another test tube. Add 2-3 drops of concentrated sulphuric acid (density 1.84 g/cm³) into each test tube. Observe liberation of

bromine and iodine gases and note their colour. Write down the equations for the reactions, if it is known that manganese dioxide converts into manganese(II) sulphate.

Note: The halogens are toxic. In order to decontaminate the glassware, add 3-5 drops of sodium thiosulphate solution to the reaction mixtures and then wash the test tubes immediately.

2. Solubility of Bromine and Iodine in Organic Solvents

Procedure. Place 2-3 drops of bromine water into one test tube and the same amount of iodine water into another test tube. Add 5-6 drops of any organic solvent into each test tube. Stir the solutions using a glass rod. Note the colour of the layers in the test tubes. (The organic solvent extracts bromine and iodine from their aqueous solutions.) What halogens can be identified by this method?

3. Oxidizing Properties of the Halogens and Their Comparative Activity

A. Oxidizing properties of the halogens

Procedure. Place 3-5 drops of chlorine water into one test tube, bromine and iodine water into the second and third test tubes. Add a few drops of hydrogen sulphide solution to chlorine water until turbidity appears. Add powdered magnesium or aluminium to bromine and iodine water. Stir the solutions by means of a glass rod and observe their decolourization. Write down the equations for all reactions. What properties display the halogens in these reactions?

B. Comparison of oxidizing properties of the halogens

Procedure. Place 3-5 drops of sodium bromide solution into one test tube and the same amount of potassium iodide into two other test tubes. Add 2-3 drops of an organic solvent into each of the test tubes. Add 3-4 drops of chlorine water into the test tube containing the bromide and into one of the test tubes containing the iodide. Add the same amount of bromine water into the last test tube containing the iodide solution. Stir the test tube contents by a glass rod and establish (by the colour of the organic solvent) which halogen is liberated in the free state in each test tube.

Recording the results. Write down the ionic and molecular equations for the reactions. In each case, specify the oxidant and the reductant. Arrange the halogens in the order of their decreasing oxidizing power. Explain this order. Can halogen molecules act as reductants? Explain your answer.

C. Oxidation of iron(II) sulphate

Procedure. Place 3-5 drops of bromine water into one test tube and the same amount of iodine water into another test tube. Add 1-2 crystals of iron(II) sulphate [Mohr's salt, $(NH_4)_2SO_4 \cdot FeSO_4 \cdot 6H_2O$] to each solution.

Recording the results. Describe your observations. Write down the equations for the reaction. In which test tube was the Fe^{2+} ion not oxidized? Write down the standard electrode potentials for the systems $Cl_2/2Cl^-$, $Br_2/2Br^-$, $I_2/2I^-$, and Fe^{3+}/Fe^{2+} and indicate in which case the reaction of oxidation of $FeSO_4$ is impossible. Is this confirmed experimentally? Will chlorine water oxidize $FeSO_4$?

4. Preparing Hydrogen Halides

A. Preparing hydrogen chloride

Procedure. Assemble an apparatus as shown in Fig. 40 and fix it in the stand. Place water (slightly coloured with blue litmus) into a porcelain dish or a crystallizer. Fill microflask *1* with sodium chloride to 1/4 its capacity and add 5-6 drops of 70% sulphuric acid solution. Close the flask immediately with a stopper provided with a gas-discharge tube *2* and lower the end of the capillary tube *5* into test tube *6*. Stopper *4* on the capillary tube should not close the test tube tightly so that air can freely escape. Collect the evolving gas into the test tube for 2-3 minutes. Hydrogen chloride fumes in air. What is the white smoke? As soon as the test tube is filled with hydrogen chloride, close it tightly with the stopper and disconnect the capillary from the apparatus (pull off rubber tubing *3*). Close quickly the capillary tube with the finger tip, overturn the test tube, and put the closed capillary tip into the water coloured with litmus. Open the capillary under water and observe the rapid suction of water into the test tube due to dissolution of the gas. Observe the colour change of litmus.

Recording the results. Draw a sketch of the apparatus. Describe your observations. Write down the equations for the reaction by which hydrogen chloride is prepared. Explain the change in the colour of litmus. Does HCl reduce sulphuric acid?

B. Preparing hydrogen bromide and hydrogen iodide

Procedure. Place 3-4 microspatulas of dry potassium (sodium) iodide into one test tube and the same amount of potassium bromide into another test tube and add 5-10 drops of saturated orthophosphoric acid. Heat the test tubes slightly. Wet a blue litmus paper in water and hold it above the mouth of the test tubes. Observe the white fume and reddening of the litmus paper. Explain your observations.

Recording the results. Write down the equations for the reactions by which hydrogen bromide and hydrogen iodide are formed. Does phosphoric acid oxidize hydrogen iodide or hydrogen bromide?

5. Comparison of Reducing Properties of Halides

A. Reduction of sulphuric acid with hydrogen halides

Procedure. Take 2-3 microspatulas: of sodium (or potassium) chloride, bromide and iodide. Place each portion into each of the three separate test tubes and add 2-3 drops of concentrated sulphuric acid (density 1.84 g/cm^3). Observe the formation of white fume in the test tubes and identify the evolving substances. Observe subsequent liberation of brown vapour of bromine and iodine in the corresponding test tubes. Establish by the smell (*caution*!) liberation of sulphur dioxide in the second test tube and of hydrogen sulphide in the third test tube.

Recording the results. Describe your observations and write down equations for each reaction in two steps: (1) exchange reaction proceeding with formation of the corresponding hydrogen halides and (2) reaction of reduction of excess sulphuric acid by hydrogen bromide and hydrogen iodide. Can sulphuric acid be reduced with hydrogen chloride? How do the reducing properties change in the series HF, HCl, HBr, HI? Explain these changes.

B. Reduction of potassium dichromate

Procedure. Place 2-4 drops of potassium dichromate solution acidified with 2 *N* sulphuric acid (1-2 drops) into each of three separate test tubes. Add 2-3 drops of potassium iodide into the first test tube, the same amount of potassium bromide into the second, and of sodium chloride solution into the third test tube. Stir the solutions using separate glass rods. The dichromate was not reduced in which test tube?

Recording the results. Write down the equations for the reactions, taking into account that potassium dichromate is reduced to chromium(III) sulphate. How does the oxidation state of the halogens change in these reactions? Describe your observations.

C. Reduction of iron(III) chloride

Procedure. Repeat the above reduction test using iron(III) chloride instead of potassium dichromate.

Recording the results. Describe your observations. In which test tube was $FeCl_3$ reduced and the halogen oxidized accordingly? Do the results of (*B*) and (*C*) agree with the relative values of standard electrode potentials of the corresponding oxidation-reduction systems (test 3*C* of the experiment)? How do the reducing properties of the halide ions change? Arrange them in the order of their increasing reducing power.

6. Specific Reactions for the Halide Ions

Procedure. Precipitation of AgCl, AgBr and AgI is the specific reaction for the halide ions. Prepare the mentioned substances by exchange reactions. Take the necessary reagents in the quantity of 4-5 drops. Add 2-3 drops of 2 *N* nitric acid to the obtained precipitates and observe their dissolution.

Recording the results. Write down the ionic and molecular equations for the reactions. Note the colour of the precipitates and observe their dissolution in nitric acid.

7. Preparing Sodium Hypochlorite

Procedure. Assemble the apparatus as shown in Fig. 22*d*. Place 10-15 drops of a 2 *N* solution of sodium hydroxide into a conical test tube and place it into a beaker with cold water. Place 2-3 crystals of potassium permanganate, 1-2 drops of water, and 3-4 drops of concentrated hydrochloric acid (density 1.19 g/cm^3) into a cylindrical test tube or a microflask provided with a stopper containing a gas-discharge tube. Fix the test tube or the microflask in the stand, lower the end of the gas-discharge tube into the sodium hydroxide solution and pass the evolving chlorine (which is liberated in the first test tube) through it for 2-3 minutes. If the evolution of chlorine is too slow, heat the reaction test tube gently over a low flame (save the solution for test 8).

Recording the results. Draw a sketch of the apparatus. Describe the observed phenomena. Write down the equation for the reaction of chlorine with sodium hydroxide (upon cooling). (Sodium chloride is produced in addition to sodium hypochlorite.) Draw the electron transfer diagram.

8. Comparing Oxidizing Properties of Hypochlorites, Chlorates, and Perchlorates

Procedure. Place 3-5 drops of potassium iodide solution into each of three test tubes. Add 2-3 drops of sodium hypochlorite NaClO solution (obtained in the previous test) to the first test tube, of potassium chlorate $KClO_3$ (or 1-2 crystals of the dry salt) to the second test tube, and of potassium perchlorate $KClO_4$ to the third test tube. In which test tube was potassium iodide oxidized in a neutral medium? (This reaction can be used to detect the ClO^- ion in the absence of stronger oxidants.) Add 2-4 drops of sulphuric acid to the second and the third test tubes. In which of them was potassium iodide oxidized in an acidic medium?

Recording the results. What phenomena were observed during the procedure? Write down the equations for all reactions, bearing in mind that the I^- ion is oxidized to I^0, while the ClO^- and ClO_3^- ions are reduced to Cl^- ion. Draw your conclusion on the oxidizing power of the anions in the series ClO^-, ClO_3^-, and ClO_4^-.

9. [Control Test]

Obtain a small amount of a dry halide salt from the instructor and dissolve it in water. Using the known reactions, identify the salt. Describe your manipulations and observations in a log-book. Write down the equations for the reactions.

EXPERIMENT 26. SYNTHESIS OF POTASSIUM CHLORATE $KClO_3$

Apparatus and reagents

Burner. Asbestos-centred gauze. Distillation flask, 50- or 100-ml. Dropping funnel. Beaker, 50-ml. Beaker, 200-ml. Graduated cylinder, 25-ml. Büchner funnel. Water-jet pump. Ring stand. Filter paper. Dropping pipette. Porcelain dish. Potassium permanganate. Ice. Solutions: potassium hydroxide, 50% solution; hydrochloric acid (density 1.19 g/cm³); sulphuric acid (density 1.84 g/cm³).

Procedure. Assemble an apparatus as shown in Fig. 41. Place a small amount of potassium permanganate into flask *1*, whose side arm is connected to gas-discharge tube via rubber tubing. Close the flask with a stopper through which a dropping funnel is inserted. Fix the flask in the stand over an asbestos-centred gauze. Place concentrated hydrochloric acid (density 1.19 g/cm³) into the dropping funnel. Pour 10 ml of a 50% solution of potassium hydroxide into 50-ml beaker *4*. Heat the solution almost to boiling and put the beaker into a wider beaker *5* containing water heated to boiling. Add sulphuric acid dropwise from the funnel into the potassium permanganate so-

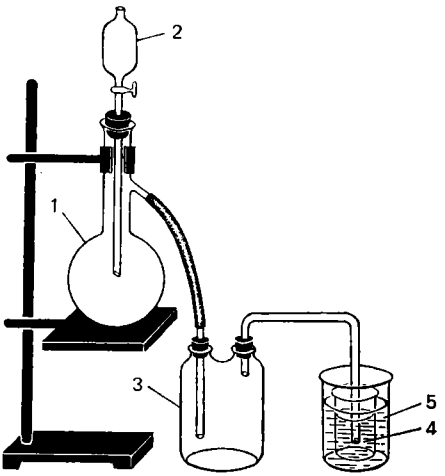


Fig. 41.
Apparatus for preparing potassium chlorate:
1–distillation flask;
2–dropping funnel;
3–safety bottle;
4–beaker with alkali;
5–beaker with water

lution in the flask. Lower the gas-discharge tube into the hot alkali solution and pass chlorine for 5-10 minutes. If the evolution of chlorine weakens, heat the flask carefully. Observe precipitation of potassium chlorate crystals. Remove the gas tube from the alkali solution, cool the solution with the crystals, and transfer the mixture onto the Büchner funnel (containing filter). Separate the crystals on the funnel, and wash them with a small amount of ice-cold water. Remove the crystals from the funnel and dry them in air between two sheets of filter paper.

Write down the equation for the reaction between chlorine and potassium hydroxide with heating. What substance, in addition to potassium chlorate, is produced?

Study the oxidizing properties of potassium chlorate. To that end, place a few crystals of the salt into a small crucible or a porcelain dish and add carefully, from a pipette, 1-2 drops of concentrated sulphuric acid. Observe the reaction. Now try the action of hydrochloric acid on the crystals. Observe the reaction. Write down the equations for the reactions.

13 Elements of Subgroup VIA

QUESTIONS AND PROBLEMS

1. Write down the electron formulas for the atoms of sulphur, selenium and tellurium in their ground and excited states.
2. In which oxidation state can sulphur be: (a) only an oxidant, and (b) a reductant? Write down the corresponding electron formulas. Give examples of reactions.

3. In what oxidation state can sulphur be both the reductant and oxidant? Give examples of the corresponding reactions.
4. How do the ionization potential and electron affinity change in the series S—Se—Te—Po? Explain these changes.
5. The molecule of S_2 is paramagnetic. Write down its electron formula. Which electron orbitals overlap to form the bond in the molecule of H_2S?
6. What substances will be obtained by the interaction of FeS with (a) hydrochloric acid, (b) concentrated nitric acid? Write down the corresponding equations.
7. Write down the equations for stepped dissociation of hydrosulphuric acid. How will the equilibria change if (a) hydrochloric acid, (b) lead(II) nitrate, or (c) alkali is added?
8. Write down the equations for the hydrolysis of the sulphides Al_2S_3 and Na_2S.
9. Write down the formulas of two sulphides insoluble in water and soluble in acid, and of two sulphides insoluble in neutral or acidic media. Write down the equations for the reactions by which these sulphides are prepared.
10. Write down the equations for reactions by which sulphur dioxide is obtained by three various methods. What is the type of hybridization of the sulphur atom in the SO_2 molecule? What is the geometrical structure of the molecule?
11. What ions are obtained when SO_2 is passed through (a) pure water, and (b) water containing Cl_2? Write down the corresponding ionic equations.
12. Which salt, K_2SO_3 or K_2SeO_3 is hydrolyzed greater in an aqueous solution of equal concentration?
13. Write down the structural formula of sodium thiosulphate and indicate the oxidation state of sulphur in this compound, and explain its instability in an acidic medium.
14. Can concentrated sulphuric acid be used as a drying agent to dry hydrogen sulphide, hydrogen bromide or hydrogen iodide? Explain your answer and write down the corresponding reaction equations.
15. Write down the structural formulas for sodium disulphate and sodium peroxydisulphate.
16. Write down the equations for reactions between sodium thiosulphate and (a) hydrochloric acid, and (b) chlorine water.
17. Write down the equation for the reaction between sodium peroxydisulphate and manganese(II) sulphate (in the presence of water).
18. Write down the ionic and molecular equations for the following reactions and complete them:

(a) $(NH_4)_2S + FeCl_2 =$
(b) $H_2S + FeCl_3 =$
(c) $H_2SO_4(conc.) + Zn =$

19. Complete the following reactions and place appropriate coefficients:

(a) $H_2S + HNO_3(conc.) =$
(b) $K_2Cr_2O_7 + Na_2S + H_2SO_4 = S + Cr_2(SO_4)_3 + \ldots$
(c) $Na_2SO_3 + Zn + HCl(dil.) = S^{2-} + \ldots$
(d) $H_2SO_3 + KMnO_4 = Mn^{2+} + \ldots$
(e) $FeSO_4 + K_2S_2O_8 = Fe^{3+} + \ldots$

Examples of Multiple-choice Questions

1. Acid was added to the salts given below. In which case is gas liberated?
(1) Na_2SO_4; (2) $CuSO_4$; (3) Na_2S; (4) Na_2SO_3; (5) $Na_2S_2O_3$.
2. What substances are obtained by the reaction of zinc and dilute sulphuric acid?
(1) $ZnSO_4 + H_2O + SO_2$; (2) $ZnSO_4 + H_2$; (3) $ZnSO_4 + S + H_2O$;
(4) $ZnSO_4 + H_2O + H_2S$; (5) $ZnSO_3 + H_2O$.

3. Which of the following sulphides is soluble in water?
(1) CaS; (2) CuS; (3) ZnS; (4) CoS; (5) NiS.
4. What is the equivalent weight of sulphur in a compound containing 50% sulphur and 50% oxygen?
(1) 32; (2) 8; (3) 16; (4) 4; (5) 5.33.
5. Specify the type of hybridization of Se orbitals in the H_2Se molecule:
(1) sp; (2) sp^2; (3) sp^3; (4) sp^2d^3; (5) no hybridization.

EXPERIMENT 27. SULPHUR

Apparatus and reagents

Test tubes, cylindrical.
Porcelain crucible.
Porcelain dish. Beaker, 200-ml. Clay triangle. Holder for micro-test tubes. Apparatus for preparing hydrogen sulphide. Apparatus for preparing sulphur dioxide gas. Asbestos-centred gauze. Forceps. Microbeaker. Filter paper. Sulphur. Copper (wire and chips).
Iron sulphide. Sodium sulphite. Zinc, granules or powder. Iron (wire and shavings). Potassium (ammonium) persulphate. Litmus paper. Carbon disulphide or benzene. Ethyl alcohol.
Solutions: bromine water; iodine water; hydrogen sulphide solution; sodium sulphide, concentrated; potassium iodide, 0.1 *N*; sodium sulphate, 0.5 *N*; mercury(I) nitrate, 0.5 *N*; nitric acid, density 1.4 g/cm³, 2 *N*; hydrochloric acid, 2 *N*, density 1.19 g/cm³; sulphuric acid, 2 *N*, 4 *N*, density 1.84 g/cm³; ammonium sulphide, 0.5 *N*; barium chloride, 0.5 *N*; iron(III) chloride, 0.5 *N*; potassium permanganate, 0.5 *N*; potassium dichromate, 0.5 *N*; manganese sulphate, 0.5 *N*; lead nitrate, 0.5 *N*; silver nitrate, 0.1 *N*; sodium thiosulphate, 0.5 *N*; sodium sulphite, 0.5 *N*; ammonium peroxydisulphate, 0.5 *N*.

1. Hydrogen Sulphide and Its Properties

A. Preparing hydrogen sulphide and its burning

Procedure. Place iron sulphide into a test tube to 1/3 its capacity, and fix it in the stand. Add 5-6 drops of hydrochloric acid (density 1.19 g/cm³) and close quickly with a stopper fitted with a gas tube (see Fig. 22*e*). Light up the gas at the tube outlet. Hold a blue litmus paper wetted with distilled water over the flame and explain the change in its colour.

Recording the results. Describe your observations. Write down the equations for the reaction of (a) formation of hydrogen sulphide; (b) its complete burning; and (c) the gas obtained by burning hydrogen sulphide with water.

Which of these reactions is oxidation-reduction one?

B. Dissolution of hydrogen sulphide in water

Procedure. Place iron(II) sulphide into a test tube and add 2-3 drops of concentrated hydrochloric acid (density 1.19 g/cm^3). Close the test tube with a stopper containing a bent gas-discharge tube (see Fig. 22*d*). Pass the liberated hydrogen sulphide into a test tube filled with a neutral litmus solution to 1/3 its capacity. Observe and explain the change of litmus colour and decide what the aqueous solution of hydrogen sulphide is. Write down the equations for dissociations of hydrosulphuric acid and the expressions of dissociation constants for its first and second steps. Write down their numerical values (see Table 7 of Appendix).

C. Reducing properties of hydrogen sulphide

Procedure. Place 5 drops of potassium permanganate and 2 drops of 2 *N* sulphuric acid into one test tube and the same amounts of potassium dichromate and sulphuric acid into another test tube. Add, drop by drop, hydrogen sulphide solution into each tube until the colour changes and cloudiness develops (precipitation of sulphur).

Recording the results. Write down the equations for the corresponding reactions, keeping in mind that MnO_4^- ion converts into Mn^{2+} ion, and $Cr_2O_7^{2-}$ ion converts into $2Cr^{3+}$ ion.

2. Preparing Sparingly Soluble Sulphides

Procedure. Place 3-4 drops of manganese sulphate into one test tube and the same amount of lead nitrate into another test tube. Add 2-4 drops of ammonium sulphide to each solution. Observe precipitation of manganese sulphide and lead sulphide. Add 2-3 drops of 2 *N* nitric acid solution to the obtained precipitates. Which sulphide dissolves? Can it be formed in an acidic medium?

Add 3-4 drops of hydrogen sulphide solution to solutions of the same manganese and lead salts in two other test tubes. In which test tube does precipitation not occur? Why?

Recording the results. Write down the ionic and molecular equations for the reactions by which manganese sulphide and lead sulphide are prepared. Indicate their colour. Write down the equation for the reaction of dissolution of MnS in the acid. Use the values of solubility products for MnS and PbS (see Table 8 of Appendix) and also the solubility product law to explain (a) the different action of H_2S and $(NH_4)_2S$ on the manganese salt; (b) precipitation of PbS in both cases. (Precipitation of black PbS is a specific reaction for S^{2-} ion.)

3. Sodium Polysulphide and Its Properties

Procedure. (*Use the hood!*) Two or thee students can carry out the experiment using one apparatus. Place 8-10 ml of concentrated sodium sulphide solution in a microbeaker and add a small quantity of finely crushed sulphur wetted preliminarily with alcohol. Boil carefully over a low flame of the burner until the solution colour changes. Separate the solution of thus prepared sodium polysulphide from unreacted sulphur in a centrifuge or allow the mixture to settle. Transfer 5-6 drops of the clear solution into a clean test tube by means of a pipette.

Add a 2 *N* hydrochloric acid solution by drops until the medium reacts acid (litmus paper). Observe precipitation of colloidal sulphur after a certain period of time. Write down the structural formulas of the sulphide and a simple polysulphide.

Recording the results. Describe the observed phenomena. Write down the equations for the reactions by which sodium polysulphide Na_2S_2 is formed and decomposed in an acidic medium (disproportionation reaction) if it is known that sulphur in the oxidation state (—I) converts into S^0 and S^{2-} ion.

4. Preparing Sulphur Dioxide and Its Dissolution in Water

Procedure. Place neutral litmus solution into one test tube and distilled water into another. Fill a microflask or a test tube with crystalline sodium sulphite to 1/3 its capacity, add 6-8 drops of 4 *N* sulphuric acid and close quickly with a stopper provided with a gas-discharge tube (see Fig. 22*d*). Pass the liberated gas into neutral litmus and into distilled water for 2-3 minutes. If the liberation of gas is not energetic, heat the flask carefully. Save the prepared aqueous solution of SO_2 for the next test 5. What properties of the aqueous solution of SO_2 indicate the litmus colour?

Recording the results. Write down the equations for the reactions by which sulphur dioxide gas is prepared, of its interaction with water (with formation of the hydrate $SO_2 \cdot H_2O$), and the equilibrium of the prepared solution:

(1) $SO_2 \cdot H_2O \rightleftarrows HSO_3^- + H^+$

(2) $HSO_3^- \rightleftarrows SO_3^{2-} + H^+$

In what direction will the equilibrium be shifted if alkali is added?

5. Oxidizing and Reducing Properties of Sulphur(IV) Compounds

A. Oxidizing and reducing properties of SO_2

Procedure. Place 3-5 drops of hydrogen sulphide water into one test tube and of iodine water into another. Add a few drops of the aqueous solution of SO_2 prepared in the previous test to both test tubes and observe the reaction.

Recording the results. Write down the equations for the corresponding reactions and indicate what properties sulphur dioxide manifests in either case.

B. Reducing properties of SO_3^{2-} ion

Procedure. Place 5-6 drops of potassium permanganate solution and 3-4 drops of 2 *N* hydrochloric acid into a test tube and add a few crystals of sodium sulphite. Observe the vanishing of colour due to the conversion of MnO_4^- into Mn^{2+}. (This reaction can be used to detect SO_3^{2-} ion in the absence of other reductants.) Into what compound has sodium sulphite converted? Since barium sulphite is soluble in nitric acid while barium sulphate is not, make sure that SO_3^{2-} ion has converted into the SO_4^{2-} ion. To do so, add 1-2 drops of 2 *N* nitric acid and the same amount of barium chloride solution to the obtained solution. What substance precipitates? Observe the reaction and write down the equations for the corresponding reactions.

6. Dehydrating Properties of Sulphuric Acid

Procedure. Draw some characters on a sheet of filter paper using a glass rod and 2 *N* sulphuric acid. Dry the paper holding it high over a burner. Observe the reaction and explain appearance of black colour on the paper. What property of concentrated sulphuric acid is demonstrated by this experiment?

7. Reaction of Sulphuric Acid with Metals

A. Reaction of dilute sulphuric acid with metals

Procedure. Place 5-8 drops of 2 *N* sulphuric acid into each of three test tubes and add 2-3 grains of zinc into the first test tube, of iron into the second and of copper into the third. If the reaction is slow, heat slightly the test tubes over a low flame of the burner.

Recording the results. In which test tube does no reaction occur? Explain your answer. Write down the equations for the reactions. Which element acts as an oxidant in these reactions?

B. Reaction of concentrated sulphuric acid with copper

Procedure. Place 1-2 copper chips into a crucible and add 5-10 drops of concentrated sulphuric acid (density 1.84 g/cm^3). Heat the crucible on an asbestos-centred gauze over a small flame. Hold a wet blue litmus paper over the crucible and expose it to the evolving gas. Observe the change of paper colour. Identify the gas by smelling it carefully.

Evaporate the liquid in the crucible, cool the remainder and dissolve in 8-10 drops of distilled water. Using a pipette, transfer a few drops of the solution to a clean test tube. Note the colour of the solution. Which ion accounts for this colour?

Recording the results. Describe your observations. Answer the questions. Write down the equation for the reaction and indicate which element in the molecule of sulphuric acid acts as an oxidant.

C. Reaction of concentrated sulphuric acid with zinc

Procedure. Place a small quantity of zinc dust into a crucible and add 5-10 drops of concentrated sulphuric acid (density 1.84 g/cm^3). Heat the crucible over a small flame and hold a sheet of filter paper wetted with a solution of lead acetate (or nitrate) over the evolving gas. Explain the appearance of a dark spot on the paper.

Recording the results. Describe your observations. Write down the equations for the reactions between concentrated sulphuric acid and zinc with formation of (a) sulphur dioxide gas; (b) sulphur, and (c) hydrogen sulphide.

8. Solubility of Barium Sulphite and Barium Sulphate in Acid

Procedure. Prepare barium sulphite and barium sulphate precipitates by exchange reactions in two separate test tubes taking 3-4 drops of the corresponding salts. Compare the solubility of barium sulphite and barium sulphate in acid. Add 1-2 drops of a 2 *N* nitric acid solution to both test tubes and observe the reaction. Can this reaction be used to differentiate between SO_3^{2-} and SO_4^{2-} ions?

Recording the results. Write down the equations for the reactions by which barium sulphite and barium sulphate are obtained, and also for the reaction by which barium sulphite is dissolved in the acid.

9. Sodium Thiosulphate and Its Properties

A. Instability of sodium thiosulphate in an acidic medium

Procedure. Place 5-6 drops of sodium thiosulphate solution $Na_2S_2O_3$ into a test tube and add 3-4 drops of 2 *N* sulphuric acid.

Recording the results. Observe precipitation of sulphur. Identify the evolving gas by its odour. Draw the structural formula of sodium thiosulphate. Write down the equation for the reaction between sodium thiosulphate and sulphuric acid. Indicate the reductant and the oxidant in the reaction.

B. Reducing properties of sodium thiosulphate

Procedure. Place 5-6 drops of bromine water into one test tube and the same amount of iodine water into another test tube. Add a few drops of sodium thiosulphate solution to both test tubes till the colour vanishes.

Recording the results. Write down the equations for the reactions, taking into account that bromine oxidizes thiosulphate to sulphate with involvement of water in the reaction (the precipitating sulphur is the product of a side reaction). Iodine oxidizes thiosulphate to tetrathionate $Na_2S_4O_6$. To what oxidation state are bromine and iodine converted in the reaction? Can chlorine water oxidize sodium thiosulphate? Explain your answer.

10. Oxidizing Properties of Peroxydisulphates

A. Oxidation of potassium iodide

Procedure. Place 3-4 drops of potassium iodide solution into a test tube and add the same amount of ammonium peroxydisulphate solution. Observe the colour change and write down the reaction equation.

B. Oxidation of chromium(III) sulphate

Procedure. Place 3-4 drops of chromium(III) sulphate solution and 2-3 drops of sulphuric acid in a test tube and add 1-2 drops of silver nitrate (catalyst). Heat the mixture over a small flame of a burner. Add 2-3 crystals of potassium (or ammonium) peroxydisulphate to the hot solution and heat again till the colour changes.

Recording the results. Write down the structural formula of ammonium peroxydisulphate and put the proper coefficients using the electron balance:

$$Cr_2(SO_4)_3 + (NH_4)_2S_2O_8 + H_2O \rightarrow (NH_4)_2SO_4 + (NH_4)_2Cr_2O_7 + H_2SO_4$$

11. [Control Test]

Obtain an unknown salt from the instructor, dissolve it in distilled water, and stir with a glass rod. Use any of the known methods to decide if the salt is a sulphite, sulphate, thiosulphate, or sulphide. Take 5-6 drops of the solution for each test.

Describe your procedure and observations. Reason your conclusion. Write down the equations for the reactions.

EXPERIMENT 28. SYNTHESIS OF SODIUM THIOSULPHATE $Na_2S_2O_3 \cdot 5H_2O$

Apparatus and reagents

Chemical balance. Asbestos-centred gauze. Büchner funnel. Water-jet pump. Water bath. Porcelain dish. Funnel, 3 cm in diameter. Erlenmeyer flask or a beaker, 100-ml. Graduated cylinder, 50-ml. Glass rod. Watch glass. Pipette. Filter paper. Sodium sulphite, crystalline. Sulphur, fine powder or sulphur flowers. Ethyl alcohol. Solutions: chlorine water; bromine water; hydrochloric acid, 2 *N*; silver nitrate, 0.1 *N*.

Procedure. Weigh out on a chemical balance 6 g of sodium sulphite on a sheet of filter paper or on a watch glass and transfer it into an Erlenmeyer flask or a beaker (100-ml). Measure out 30 ml of distilled water with a graduated cylinder and add to sodium sulphite. Place the flask (beaker) on an asbestos-centred gauze over a burner and heat slowly until the salt dissolves completely. Weigh out 3 g of sulphur (powder or flowers), wet it with a few drops of alcohol, and transfer into the flask containing sodium sulphite solution. Stir the mixture using a glass rod and heat the suspension over a small flame for 10-15 minutes till the sulphur dissolves almost completely. If the liquid volume decreases appreciably, add water. Using a small filter, separate the hot solution from the remaining sulphur into a porcelain dish. Place the dish in a water bath and evaporate the solution until crystallization begins. Allow the solution to cool. If crystals do not precipitate from an oversaturated solution, drop a seeding crystal of sodium thiosulphate. Separate the precipitated crystals on a Büchner funnel, transfer them onto filter paper and dry between two sheets of paper. Weigh the dry crystals and determine the yield in per cent of the initial sodium sulphite. Dissolve a few crystals of the salt in a test tube and study some properties of sodium thiosulphate: (1) its instability in an acidic medium; (2) the reducing properties of the thiosulphate (tests 10 *A* and 10 *B*). Write down the equations for the reactions. Draw the structural formula of sodium thiosulphate.

14 Elements of Subgroup VA

QUESTIONS AND PROBLEMS

1. Write down the equations for the reactions by which nitrogen is prepared by (a) reducing potassium nitrate with iron; (b) decomposing ammonium nitrite; (c) oxidizing ammonia. Indicate the oxidant and reductant in each reaction.
2. Draw the outermost electron layer in the atoms of nitrogen, phosphorus, and arsenic in their ground and excited states.
3. Knowing that the nitrogen molecule is diamagnetic draw its electron configuration using the valence bond and molecular orbital methods. How many bonds are there in the N_2 molecule and what is their character?
4. Knowing the relative electronegativity of the atoms of F, Cl, Na and N, indicate the shift of the electron pairs and the corresponding oxidation state of each element in the molecules NF_3, NCl_3, and Na_3N. How will the indicated nitrides react with water? Write down the reactions.
5. What reagents should be used to prepare ammonia from (a) nitrogen, (b) ammonium salt, (c) nitric acid, (d) aluminium nitride? Write down the equations for the reactions.
6. What is the hybridization type of the atomic orbitals in nitrogen during formation of ammonia molecule? What is the geometrical configuration of the molecule? Draw the electron cloud overlapping in this molecule.
7. Write down the equilibrium in an ammonia solution and the expression for the equilibrium constant, taking into account that NH_3 is a better acceptor of the proton H^+ than the H_2O molecule.
8. What is the number and character of bonds (covalent, ionic, donor-acceptor) in the NH_3 molecule? In NH_4^+ ion? Draw their electron formulas. What is the covalence of nitrogen in NH_4^+ ion?
9. Explain the formation of the molecule NH_4Cl from ammonia and hydrogen chloride. What is the type of interatomic bonds in this molecule? Which element is the complexing agent? Which elements are donors, acceptors and ligands?
10. Write down the equations for the reactions specific for ammonia: addition, substitution, oxidation, and complex formation.
11. Write down the molecular and ionic equations for the reaction between ammonia and phosphoric acid.
12. Write down the equations for the reactions of thermal decomposition of the nitrite, nitrate and carbonate of ammonium.
13. Write down the equations for the hydrolysis of (a) ammonium chloride. (b) ammonium carbonate.
14. Write down the formulas of the oxides of nitrogen in the oxidation states +I, +II, +III, +IV, and +V, and the equations for the reactions by which they are prepared.
15. Write down the electron schemes for the N_2O molecule using the valence bond method, and of the NO molecule using the molecular orbital method. What is the covalence of each nitrogen atom in the N_2O molecule? Is the NO molecule para- or diamagnetic? Explain your answer.
16. Which of the nitrogen oxides will react with KOH? Write down the equations for the corresponding reactions.
17. Write down the equations for the subsequent reactions by which nitric acid is prepared from ammonia in industry.
18. Give the electron formula for the nitric acid molecule, keeping in mind that the interatomic bonds in it can be both covalent and donor-acceptor. What is the covalence of nitrogen in the nitric acid molecule?

19. Write down the equations for the reactions between (a) concentrated nitric acid and silver or phosphorus; (b) dilute nitric acid and copper or magnesium.
20. Write down the equations for the thermal decomposition of sodium nitrate, copper nitrate and mercury(II) nitrate.

21. (a) $NO_2^- \rightarrow NO_3^-$ (c) $N^{-3} \rightarrow NH_4^+$
(b) $NO_2^- \rightarrow NO$ (d) $NO_2 \rightarrow NO_3^- + NO$

By which reactions can these conversions be accomplished? Write down the molecular equations for the corresponding reactions.
22. Write down the equations for the reactions by which phosphorus is prepared from natural calcium phosphate.
23. Write down the equations for hydrolysis of phosphorus(III) iodide and phosphorus chloride.
24. Write down the empirical and structural formulas for the following acids: (a) phosphoric; (b) diphosphoric; (c) phosphorous, if it is known that the last acid is dibasic. What is the covalence and oxidation state of phosphorus in each case?
25. How does the electronegativity change in the atoms of arsenic, antimony, and bismuth, and how do the stability and the reducing power of the compounds AsH_3, SbH_3 and BiH_3 change in this connection?
26. Which of the following oxides has more pronounced basic properties? In which of them are the acidic properties stronger? Which of them is a stronger oxidant, a stronger reductant?

As_2O_3 As_2O_5
Sb_2O_3 Sb_2O_5
Bi_2O_3 Bi_2O_5

What factors are important for these properties?
27. Write down the ionic and molecular equations for the following reactions: (a) preparing hydroxides of $As^{+}III$, $Sb^{+}III$, $Bi^{+}III$; (b) interaction of these hydroxides with excess alkali or acid. What properties are manifested by these hydroxides?
28. The reaction between Na_3AsO_4 and H_2S in the presence of hydrochloric acid gives As_2S_3 and sulphur in addition to As_2S_5. Explain this reaction and illustrate your answer by the equations of two corresponding reactions.
29. Write down the formulas for the antimony(III) oxychloride, bismuth(III) oxynitrate, and the reactions for their formation during hydrolysis of the corresponding salts.
30. Which elements of the arsenic subgroup in the oxidation state +III form thiosalts? Write down the formulas of these thiosalts, their names, and equations for the reactions by which they are prepared (reactions between the corresponding chlorides and excess ammonium sulphide).
31. In what substance can the following be dissolved:
(a) $Sb(OH)_3$ and $Bi(OH)_3$? (b) Sb_2S_3 and Bi_2S_3? Write down the equations for the corresponding reactions.
32. Sb^{3+} and Bi^{3+} ions are present in a solution. Which reagents can be used to separate these ions? Write down the equations for the corresponding reactions.
33. How can the following conversions be accomplished?

(a) $BiOCl\downarrow \rightarrow Bi^{3+}$ (c) $SbS_3^{3-} \rightarrow Sb_2S_3\downarrow$
(b) $[Sb(OH)_6]^{3-} \rightarrow Sb^{3+}$ (d) $Bi^{3+} \rightarrow Bi_2O_5$

Write down the molecular equations for the above processes.
34. Complete the following equations and place proper coefficients:

(a) $Bi_2O_5 + H_2SO_4 + H_2O_2 =$ (b) $NaBiO_3 + FeSO_4 + NaOH =$

Examples of Multiple-choice Questions

1. Which of the following substances is mainly prepared by the reaction between zinc and excess dilute nitric acid?
(1) NH_3; (2) NO_2; (3) H_2; (4) NH_4NO_3; (5) NO.
2. Which substance (taken in excess) can separate Sb^{3+} and Bi^{3+} ions in a solution?
(1) H_2SO_4 (dilute); (2) NaOH; (3) H_2S; (4) $(NH_4)_2S$; (5) Na_2SO_4.
3. What substances are prepared by the reaction between H_2O and Mg_3N_2?
(1) N_2 and $Mg(OH)_2$; (2) NH_3 and MgO; (3) MgO + NO + H_2; (4) NH_3 + + $Mg(OH)_2$; (5) N_2O_3 + H_2Mg.
4. Which of the following aqueous solutions of the same molar concentration and at the same temperature has the lowest pH value?
(1) $Bi(NO_3)_3$; (2) $SbCl_3$; (3) Na_3PO_4; (4) $AsCl_3$; (5) PCl_3.
5. Determine the sum of all coefficients in the right and the left parts of the equation:

$$Bi_2S_3 + HNO_3 = Bi_2(SO_4)_3 + NO_2 + H_2O$$

(1) 48; (2) 18; (3) 72; (4) 12; (5) 62.

EXPERIMENT 29. NITROGEN

Apparatus and reagents

Apparatus for preparing nitrogen(II) oxide. Crystallizer or a porcelain dish. Porcelain crucible. Microflask. Splint. Glass rod. Lead nitrate. Ammonium acetate. Potassium nitrate. Ammonium chloride. Ammonium sulphate. Magnesium powder. Potassium nitrite. Silver nitrate. Copper shavings. Slaked lime. Indicators: red litmus paper, phenolphthalein, litmus red. Solutions: bromine water; ammonium chloride, 0.5 *N*, saturated; potassium nitrite, 0.5 *N*, saturated; potassium iodide, 0.1 *N*; aluminium sulphate, 0.5 *N*; potassium permanganate, 0.5 *N*; potassium dichromate, 0.5 *N*; nitric acid (density 1.4 g/cm^3 and 1.12 g/cm^3); sulphuric acid, 2 *N*; hydrochloric acid (density 1.19 g/cm^3); sodium hydroxide, 2 *N*; ammonia solution, 2 *N* and 25%.

1. Preparing Ammonia and Its Reaction with Water and Hydrogen Chloride

Procedure. Place 3-4 microspatulas of ammonium sulphate and the same amount of slaked lime into a porcelain crucible and stir the mixture thoroughly using a glass rod. Transfer a small portion of the mixture into a cylindrical test tube (about 1/2 its capacity). Smell the odour of ammonia. Fix the test tube in a stand, close it with a stopper provided with a gas-discharge tube. Lower the tube end into a conical test tube filled with water to about 2/3 its capacity

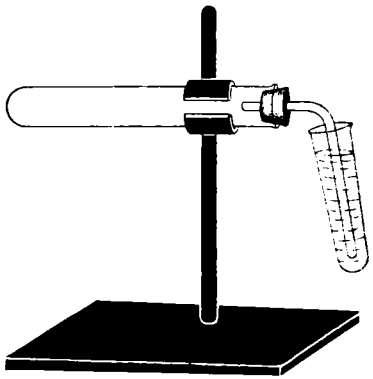


Fig. 42.
Apparatus for preparing ammonia

(Fig. 42). Heat the test tube over a small flame for 3-5 minutes, passing the liberated ammonia into water. Close the conical test tube with a stopper and save the obtained solution for the next test. Hold a glass rod wetted with concentrated hydrochloric acid (density 1.19 g/cm^3) to the outlet of the gas tube. Next, hold a wetted red litmus paper to the outlet.

Recording the results. Describe your observations and explain them. Write down the equations (a) for the reaction of preparing ammonia, (b) for the reaction between ammonia and water during which the ammonium ion is partly formed*:

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

The process can be regarded as protonization of the ammonia molecule because the latter is a better acceptor of the proton than the water molecule.

2. Equilibrium in Aqueous Ammonia Solution

Procedure. Divide the ammonia solution prepared in the previous test 1 into two test tubes. Add a drop of phenolphthalein to one test tube and note the colour. The presence of which ions accounts for the colour? Add 3-4 microspatulas of ammonium chloride and stir the mixture. How does the intensity of the colour change? Explain. Add 5-6 drops of aluminium sulphate to the ammonia solution in another test tube. Note the disappearance of ammonia odour.

Recording the results. Write down (a) the equation of equilibrium in an ammonia solution; (b) the molecular and ionic equations for the interaction between aluminium sulphate and ammonia solution.

* Aqueous ammonia solution is commonly expressed by the formula NH_4OH, although a better way is $NH_3 \cdot H_2O$ because there is a hydrogen bond in this compound. The molecule NH_4OH has not been detected.

Indicate the direction in which the equilibrium in the ammonia solution shifts after ammonium chloride is added to it. Indicate the shift of equilibrium after adding aluminium sulphate. How does the concentration of the OH^-, NH_4^+ ions and of NH_3 change in this system? In what direction will the equilibrium of the system shift if hydrochloric acid is added? Explain your answers.

3. Reducing Properties of Ammonia

Procedure. Place 3-4 drops of bromine water into the first test tube, the same amount of potassium permanganate solution into the second and of potassium dichromate solution into the third test tube. Add 3-5 drops of 25% ammonia solution to each test tube and heat the solutions slightly till their colours change.

Recording the results. Write down the equations for the corresponding reactions, taking into account that in each particular case ammonia solution is mainly oxidized to the molecular nitrogen, $KMnO_4$ is reduced to MnO_2, while $K_2Cr_2O_7$ to Cr_2O_3. Note the colour change in all cases.

4. Hydrolysis of Ammonium Salts

Procedure. Place 5-6 drops of a neutral litmus solution into each of three test tubes. Add 2-3 microspatulas of crystalline ammonium chloride into one test tube, of ammonium nitrate into the other, and of ammonium acetate into the third test tube. Stir each solution by a separate glass rod.

Recording the results. Note the change of litmus colour in each solution. Write down the ionic and molecular equations for the reactions of hydrolysis of the salts*.

5. Identification of NH_4^+ Ion

Procedure. Place 2-3 drops of an ammonium salt into a test tube and add the same amount of a 2 *N* sodium (or potassium) hydroxide solution. Heat the test tube slightly and hold a wet red litmus paper over its mouth. Identify the evolving ammonia and OH^- ion by the odour and the change of litmus colour.

Recording the results. Write down the ionic and molecular equations for the reaction. Can this reaction be used to detect NH_4^+ ion in the presence of KCl or $NaNO_3$? Reason your answer.

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* The reaction of hydrolysis of ammonium salts can be regarded as the reaction of deprotonization of the NH_4^+ ion:
$NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$

6. Nitrogen Oxide and Nitrogen Dioxide. Their Properties

Procedure. Place water in a small crystallizer or a porcelain evaporating dish. Fill a conical test tube with water, close it with a finger tip, turn upside down, and place into a crystallizer. Open the test tube under water so that water does not flow out of it and no air enters.

Place 2-3 small pieces of copper shavings and 2-4 drops of dilute nitric acid (density 1.12 g/cm^3) into a microflask with a delivery tube (see Fig. 22*c*). Fasten the flask in the stand, and if the reaction is slow, heat gently over a small flame. Lower the delivery tube into the crystallizer and put the conical test tube on the tube end. As soon as the test tube is filled with the evolving gas to 3/4 its capacity (some water should remain in it), press the finger tip to seal the mouth of the test tube under water, remove it from water, and turn into the normal position. Now release the finger and admit air for 1-2 seconds: observe the gas in the test tube growing brown. (Observe it against the background of white.)

Close the test tube with the finger tip again, shake several times until the gas is completely absorbed by water. Open the test tube and observe evolution of the brown gas again and its absorption by water on repeated shaking. Add 1-2 drops of a neutral litmus solution and judge on the reaction of the medium by the change of the litmus colour.

Recording the results. Describe the observed phenomena. Write down the equations for the following reactions:

(a) preparing nitrogen(II) oxide by the reaction between copper and dilute nitric acid;

(b) oxidation of nitrogen(II) oxide to the dioxide, and the reaction of its dimerization.

Write down the structural and electron formulas for these oxides. How can the easy oxidability of NO and the ability of NO_2 to polymerize be explained?

(c) formation of nitric acid and nitrogen(II) oxide by the reaction between NO_2 and water.

7. Nitrogen(III) Oxide and Nitrous Salts

A. Preparing nitrogen(III) oxide and its decomposition

Procedure. Place 3-4 drops of a saturated potassium nitrite solution into a test tube and add a drop of 2 *N* sulphuric acid solution. Note the blue colour of N_2O_3 which is the anhydride of an unstable nitrous acid. Explain the formation of a brown gas above the solution.

Recording the results. Write down the equations for the reactions between potassium nitrite and sulphuric acid proceeding with formation of N_2O_3 and the reaction of its decomposition into NO and NO_2 (disproportionation reaction).

B. Reducing and oxidizing properties of nitrites

Procedure. Place 3-4 drops of potassium iodide into one test tube, of potassium permanganate into the other, and of potassium dichromate into the third test tube. Add 2-4 drops of a 2 *N* sulphuric acid and 4-5 drops of potassium nitrite into each test tube.

Recording the results. Observe the change in the solution colour in each particular case. Write down the equations for the reactions taking into consideration that potassium nitrite is reduced to NO, potassium permanganate converts into manganese(II) sulphate, and potassium dichromate into chromium(III) sulphate. Into what compound is potassium nitrite converted in these reactions? Indicate in which reaction potassium nitrite acts as an oxidant and in which as a reductant?

Either of the three experiments can be used for detecting NO_2^- ion in the presence of NO_3^- ion (provided other reducing or oxidizing agents are absent).

8. Oxidizing Properties of Nitric Acid

Procedure. Place 3-4 drops of concentrated nitric acid (density 1.4 g/cm^3) into a test tube and add a piece of copper shaving. Place 2 drops of nitric acid (density 1.12 g/cm^3) into another test tube and add two drops of water. Stir the solution by a glass rod and add a piece of copper shaving as well. Heat slightly the test tube containing the dilute nitric acid. Hold both test tubes against the background of white. Observe the different course of the reactions in the test tubes.

Recording the results. What gas is liberated in the first and the second test tube? Write down the equations for the corresponding reactions. How can the slight yellowing of the gas liberated in the second test tube at the beginning of the reaction be explained?

9. Oxidizing Properties of Nitrates

Procedure. Place 5-10 drops of a 0.5 *N* potassium nitrate solution and the same amount of concentrated alkali solution into a crucible. Add 2-3 microspatulas of powdered aluminium or magnesium. Place the crucible on an asbestos gauze and heat carefully without boiling. Hold a wet red litmus paper over the vapour liberated from the crucible. Identify ammonia by the odour (*caution*!) and by the blue

colour of the litmus paper. This reaction can be used to detect the NO_3^- in the absence of NO_2^- or NH_4^+ ions.

Recording the results. Note the observed phenomena. Write down the equation for the reaction of Mg or Al oxidation with potassium nitrate in an alkaline medium bearing in mind that aluminium is oxidized in a strongly alkaline medium to give $[Al(OH)_6]^{3-}$. What compound does magnesium form under these conditions?

10. Thermal Decomposition of Nitrates

All nitrates are decomposed on heating to liberate free oxygen. When in the molten state, nitrates therefore act as strong oxidants. Nitrates of the alkali metals are thereby converted into nitrites, while nitrates of the rare earth and heavy metals are decomposed with formation of their oxides and nitrogen dioxide. Nitrates of low-active metals with a positive electrode potential are decomposed to liberate free metals and nitrogen dioxide. Intramolecular oxidation-reduction reactions occur in all these cases.

A. Decomposition of potassium nitrate

Procedure. Place 3-4 crystals of potassium nitrate into a cylindrical test tube and fix it in a vertical position in the stand over a burner. Heat until the salt melts and gas bubbles evolve. Put a glowing splint into the test tube. What gas is liberated? Stop heating when no more gas bubbles evolve. Prove the formation of potassium nitrite during decomposition of the nitrate. To do so, cool the test tube, add 4-6 drops of water and dissolve the solid stirring it with a glass rod. Place 2-3 drops of the obtained solution into each of two test tubes one of which contains 3-4 drops of potassium iodide solution acidified with 2 drops of 2 *N* sulphuric acid, and the other contains 3-4 drops of acidified potassium permanganate solution. Observe the colour change in the test tubes. Try the action of KNO_3 on KI.

Recording the results. Write down the equations for the reactions.

B. Decomposition of lead nitrate

Procedure. Place 1-2 microspatulas of dry lead nitrate into a cylindrical test tube and fix it in the horizontal position in the stand. Heat carefully and note the colour of liberated gases.

Recording the results. Draw your conclusion on the composition of the gaseous products of lead nitrate decomposition. What gas (in addition to oxygen) is liberated? What is the remainder in the test tube? Note its colour and write down the formula of the compound. Write down the equation for the reaction of decomposition of lead nitrate. Indicate the oxidant and the reductant.

C. Decomposition of silver nitrate

Procedure. Place a few crystals of silver nitrate into a cylindrical test tube, fix it in the stand in the horizontal position and heat over a small flame until the salt has completely decomposed. Note the colour of the evolving gases.

Recording the results. What gases are liberated during decomposition of silver nitrate? Write down the equation for the reaction, if it is known that metal silver is also produced in the reaction.

11. (Control Test)

Procedure. Obtain an unknown salt from the instructor and dissolve it in a small quantity of water. Stir the mixture thoroughly using a glass rod. Divide the obtained solution into three portions and place each portion into a separate test tube. Use the specific reactions to detect NH_4^+ in the first test tube, NO_2^- in the second test tube, and NO_3^- in the third test tube. Write down the equations for the reactions and the observed phenomena which confirm the presence or absence of this or that ion in a given solution. Identify the salt you have obtained from the instructor. Is it an ammonium salt, a nitrite or a nitrate?

EXPERIMENT 30. SYNTHESIS OF POTASSIUM NITRITE

Apparatus and reagents	
Chemical balance. Iron crucible. Stirrer. Clay triangle. Crucible tongs. Iron plate. Goggles. Flask, 200-ml. Beakers (four). Porcelain mortar. Porcelain dish. Water bath.	Funnel. Büchner funnel and a distillation flask. Porcelain crucible. Test tubes. Lead, granules. Potassium nitrate. Solutions: sulphuric acid (density 1.84 g/cm³); nitric acid (density 1.2 g/cm³); potassium permanganate, 0.5 *N*.

Procedure. Potassium nitrite is obtained from potassium nitrate in this experiment by reacting it with lead at a temperature over 400°C. When handling molten KNO_3 and KNO_2, wear goggles. The hot crucibles should be handled by crucible tongs; the crucibles should be placed only on metal gauze or in a clay triangle in the stand ring.

Write down the equation for the reaction, bearing in mind that lead is oxidized in this reaction to PbO.

Weigh out 15 g of lead on a chemical balance. Calculate the necessary amount of potassium nitrate and weigh out 1.5 times the calculated amount. Transfer the potassium nitrate into an iron crucible in the stand and heat until the salt melts. Continue heating and add

lead in small portions, stirring the mixture thoroughly using an iron stirrer. Continue heating with stirring for 30-40 minutes until all lead is oxidized. Using the tongs, remove the crucible from the clay triangle and pour the molten mixture in a thin layer on an iron plate. Cool the melt, take small portions of it and triturate them in a mortar and transfer into a beaker. Add 15-25 ml of boiling water, stir well using a glass rod (take care as not to break the glass beaker). Allow the mixture to settle, and decant the liquid through a filter into another beaker (see Fig. 23).

Repeat leaching 3-4 times, each time adding the same amount of boiling water with stirring the solution and decanting it after settling. Transfer the washed residue (containing lead oxide) and the filtrate onto a filter and wash 2-3 times with hot water. Transfer the filtrate containing potassium nitrite and unreacted potassium nitrate into a porcelain dish and evaporate on a water bath to the volume not exceeding 20-25 ml. Cool the potassium nitrite solution and transfer it carefully into another porcelain dish. Transfer the unreacted crystals of potassium nitrate onto a Büchner funnel, remove moisture, and dry the crystals between filter papers. Handle potassium nitrate over to the instructor. Evaporate the solution of potassium nitrate in a porcelain dish to dryness on a water bath and put the dish in the stand ring on an asbestos-centred gauze. Melt the salt over a high flame. Pour carefully the melt on an iron plate. When the melt cools, break it into pieces, weigh, and determine the yield of KNO_2 with respect to lead (in per cent).

Prepare a small amount of the solution and study the properties of the obtained potassium nitrite by (1) acting on it with concentrated sulphuric acid, (2) by reducing potassium permanganate with it in an acid medium, and (3) by oxidizing potassium iodide with it.

Describe your observations and write down the reaction equations.

EXPERIMENT 31. PHOSPHORUS

Apparatus and reagents

Crucible. Water bath. Glass rods. Platinum loop. Red phosphorus. Calcium phosphide. Sodium phosphate. Sodium dihydrogen phosphate. Sodium-ammonium hydrogen phosphate. Cobalt nitrate. Copper oxide. Phosphorus(V) chloride (or bromide). Phosphorus(III) chloride. Indicators: litmus paper, blue; litmus solution, neutral. Solutions: nitric acid, density 1.4 g/cm^3; hydrochloric acid, 4 *N*; calcium chloride, 0.5 *N*; sodium hydrogen phosphate, 0.5 *N*; iron(III) chloride, 0.5 *N*; aluminium sulphate, 0.5 *N*; sodium acetate, 0.5 *N*; saturated solution of ammonium molybdate acidified with concentrated nitric acid; mercury(II) nitrate.

1. Preparing Phosphine

Procedure. (*Use the hood, because phosphine is poisonous*). Place 15 drops of a 4 *N* hydrochloric acid into a crucible and, using forceps, add 2-3 small lumps of calcium phosphide. Observe evolution of gas and its ignition in air.

Recording the results. Calcium phosphide Ca_3P_2 reacts with acid to give mainly gaseous hydrogen phosphide PH_3 (phosphine) and partly liquid diphosphane P_2H_4. Write down the equations for the reaction between calcium phosphide and hydrochloric acid and for hydrogen phosphide burning in air.

2. Preparing Orthophosphoric Acid

Procedure. Place a small amount of red phosphorus into a test tube (not more than a microspatula) and add 3-5 drops of concentrated nitric acid (density 1.4 g/cm^3). Fix the test tube in a stand in an inclined position and heat slightly over a low flame until gas liberation is started. Stop heating then. Allow the test tube to cool and carry out the specific reaction for PO_4^{3-} ion with ammonium molybdate:

$$H_3PO_4 + 12(NH_4)_2MoO_4 + 21HNO_3 = (NH_4)_3H_4[P(Mo_2O_7)_6] + 21NH_4NO_3 + 10H_2O$$

To do so, place 5-6 drops of a saturated ammonium molybdate solution acidified with nitric acid into a cylindrical test tube and add a drop of the solution obtained in this experiment. Heat the test tube in a water bath. Precipitation of a yellow substance indicates formation of orthophosphoric acid. This reaction is used for detecting PO_4^{3-} ion.

Recording the results. Write down the equations for the following:
(a) the reaction for preparing orthophosphoric acid, taking into account that nitrogen(II) oxide is liberated as a by-product;
(b) stepped dissociation of orthophosphoric acid;
(c) the reaction of detection of PO_4^{3-} ion using ammonium molybdate solution.

3. Orthophosphates of Certain Metals

A. Preparing calcium hydrogen phosphate

Procedure. Place 4-5 drops of calcium chloride solution in a test tube and add the same amount of sodium hydrogen phosphate Na_2HPO_4 solution.

Recording the results. Note the colour of the precipitate. Write down the ionic and molecular equations for the reaction.

B. Precipitating iron phosphate and aluminium phosphate in the presence of sodium acetate

Procedure. Place 3-4 drops of iron(III) chloride solution into one test tube and the same amount of aluminium sulphate (or chloride) into another test tube. Add 2-3 drops of sodium acetate and sodium hydrogen phosphate into each test tube. Note the colour of the precipitates.

Recording the results. Neutral phosphates of iron and aluminium, insoluble in acetic acid, are obtained in solutions of iron(III) and aluminium salts buffered with sodium acetate:

$$Me^{3+} + HPO_4^{2-} + CH_3COO^- = MePO_4 \downarrow + CH_3COOH$$

Write down the ionic and molecular equations for the reactions.

4. Hydrolysis of Certain Phosphorus Compounds

A. Hydrolysis of sodium orthophosphates

Procedure. Place 5-6 drops of a neutral litmus solution into each of three test tubes. Save one of them as a reference, add 3-4 crystals of sodium phosphate into the second, and the same amount of sodium dihydrogen phosphate into the third test tube. Mix thoroughly the contents in the second and the third test tubes by separate glass rods to ensure complete dissolution of the salts. Note the colour change of litmus compared with the colour in the reference test tube.

Recording the results. The increase in concentration of which ions causes the change in litmus colour during dissolution of sodium phosphate and sodium dihydrogen phosphate? Write down the ionic and molecular equations for the first step of hydrolysis of sodium phosphate.

The solution of NaH_2PO_4 is acid because the first of the following two reactions:

1. $H_2PO_4^- \rightleftarrows H^+ + HPO_4^{2-}$
2. $H_2PO_4^- + H_2O \rightleftarrows H_3PO_4 + OH^-$

(the dissociation of $H_2PO_4^{2-}$ ion) is more intense than the hydrolysis of this ion due to formation of the electrolyte HPO_4^{2-} which is weaker than H_3PO_4 ($K_{dis\ HPO_4^{2-}} = 4.5 \times 10^{-12}$; $K_{1\ H_3PO_4} = 7.9 \times 10^{-3}$).

B. Hydrolysis of phosphorus halides

Procedure. Place 3-5 drops of phosphorus(V) chloride (or bromide) in a test tube and add the same amount of distilled water. Observe liberation of gas. Hold a wetted blue litmus paper over the test-tube mouth. Observe the colour change. Test the action of a saturated am-

monium molybdate solution on the obtained solution (as instructed in test 2 of this Experiment). Describe your observations.

Repeat the experiment with phosphorus(III) halide. Phosphorous acid H_3PO_3 and hydrogen halide are obtained during hydrolysis. The acid can be detected by adding 2-3 drops of $Hg(NO_3)_2$ to the solution in the test tube. Precipitation of a grey substance (finely dispersed metallic mercury) indicates the presence in the solution of phosphorous acid:

$$H_2O + Hg(NO_3)_2 + H_3PO_3 = Hg + H_3PO_4 + 2HNO_3$$

Recording the results. What are the products of hydrolysis of the halides of phosphorus(V) and phosphorus(III)? Write down the equations for the hydrolysis reactions.

5. Preparing Phosphate Pearls

Procedure. Place crystals of sodium-ammonium hydrogen phosphate $NaNH_4HPO_4 \cdot 4H_2O$ on the first piece of filter paper, powdered cobalt nitrate and powdered copper oxide on the second and third pieces, respectively. Heat a platinum loop in the flame of a burner and touch with it the salt crystals. Introduce the loop into the flame to melt them. Observe the decomposition of the salt with liberation of ammonia, water vapour, and formation of coloured sodium metaphosphate pearl. Touch the cobalt salt with the hot pearl and heat again in the oxidizing flame of the burner. Observe the colour of the pearl in the hot state and after cooling.

Clean the platinum loop and repeat the experiment taking copper oxide instead of the cobalt salt.

Note: To clean the platinum loop strike the pearl slightly with a glass rod, or crush it with fingers. Heat the loop in the flame and wash with hydrochloric acid.

Recording the results. Write down the equations for the following:

(a) decomposition of sodium-ammonium hydrogen phosphate;

(b) reaction of copper oxide with sodium metaphosphate giving the double salt of orthophosphoric acid $CuNaPO_4$;

(c) reaction of cobalt nitrate with sodium metaphosphate yielding the double salt $CoNaPO_4$ and unstable nitric acid anhydride N_2O_5.

EXPERIMENT 32. ANTIMONY. BISMUTH

Apparatus and reagents

Test tubes. Porcelain crucible.
Glass rods. Antimony and bismuth (solid and powder). Sodium bismuthate.
Solutions: antimony chloride, 0.5 *N* and saturated;
sodium hydroxide, 0.5 and 2 *N*;
hydrochloric acid, 2 *N*, density 1.19 g/cm^3;
nitric acid, density 1.4 g/cm^3, 2 *N*;
sulphuric acid, 2 *N*; ammonium sulphide (or sodium sulphide), 0.5 *N*;
bismuth nitrate, 0.5 *N*;
bismuth chloride, 0.5 *N*;
tin(II) chloride, 0.5 *N*; manganese sulphate, 0.5 *N*; potassium iodide, 0.1 *N*;
potassium permanganate, 0.5 *N*;
hydrogen sylphide solution; bromine water

1. Reaction of Antimony and Bismuth with Nitric Acid

Procedure. Place 2-3 grains of antimony into one cylindrical test tube and of bismuth into the second test tube. Add 4-5 drops of nitric acid (density 1.4 g/cm^3) to antimony, and the same amount of 2 *N* nitric acid to bismuth. (Concentrated nitric acid passivates bismuth.) Fix the test tubes in the stand and heat carefully (one after another). Observe metal dissolution and liberation of gases.

Recording the results. Write down the reaction equations. taking into consideration that antimonic acid H_3SbO_4* and bismuth(III) nitrate are the products of the reactions. Nitric acid is reduced to NO in both cases.

2. Hydroxides of Antimony(III) and Bismuth(III) and Their Properties

Procedure. Place 3-4 drops of antimony(III) chloride solution into two separate test tubes and the same amount of bismuth nitrate solution into two other test tubes. Add 3-5 drops of 2 *N* alkali solution to all four test tubes to precipitate the corresponding hydroxides. Add a few drops of 2 *N* hydrochloric acid to one of the test tubes containing antimony hydroxide and of alkali to the other test tube. Observe dissolution of the precipitates. Act similarly with the precipitates of bismuth hydroxide but use nitric acid instead of hydrochloric acid. Does the $Bi(OH)_3$ precipitate dissolve in both test tubes?

Recording the results. Describe your observations and conclude on the properties of the hydroxides of antimony and bismuth. Write down the ionic and molecular equations for the reactions by which

* The obtained white substance has actually a more complicated composition $x Sb_2O_5 \cdot y H_2O$.

these hydroxides are obtained, and their reactions with acid and alkali (antimony hydroxide reacts with excess alkali to give a complex anion $[Sb(OH)_6]^{3-}$). In which medium is this anion more stable? In which medium is Sb^{3+} cation stable?

3. Hydrolysis of Antimony(III) and Bismuth(III) Salts

Procedure. Place 3-5 drops of 0.5 *N* solution of antimony(III) chloride into one test tube and the same amount of bismuth(III) chloride into the other test tube and add 5-10 drops of water to both. Stir the solutions using glass rods and observe cloudiness and further precipitation of basic salts. (To accelerate precipitation, rub the test tube wall with the tip of the glass rod.)

Recording the results. Write down the ionic and molecular equations for the hydrolysis of chlorides of antimony and bismuth with formation of the basic salts $Sb(OH)_2Cl$ and $Bi(OH)_2Cl$. These salts split off water and convert into antimony oxychloride SbOCl and bismuth oxychloride BiOCl, respectively. Which of the salts is hydrolyzed greater? Reason your answer.

4. Sulphides of Antimony(III) and Bismuth(III) and Their Properties

A. Preparing sulphide and thiosalt of antimony(III)

Procedure. Place 1-2 drops of antimony trichloride solution into a test tube and add 5-8 drops of hydrogen sulphide solution. Note the colour of precipitated antimony sulphide. (This reaction is a qualitative test for detection of Sb^{3+} ion in the absence of bismuth ions and ions of other metals giving sparingly soluble sulphides in an acidic medium.) Allow the solution to settle, remove the excess liquid by a pipette of filter paper, and add 4-5 drops of ammonium sulphide or sodium sulphide solution. Stir the mixture using a glass rod and observe dissolution of the precipitate to give the salt of thioantimonious acid $(NH_4)_3SbS_3$. Add 5-6 drops of 2 *N* hydrochloric acid to the obtained solution, heat slightly, and observe precipitation of antimony(III) sulphide again. What happens to the thiosalt in the acidic medium?

Recording the results. Write down the ionic and molecular equations for the reactions by which antimony(III) sulphide and the salt of thioantimonious acid are prepared, and by which the thiosalt is decomposed in acidic medium.

B. Bismuth sulphide and its properties

Procedure. Place 1-2 drops of a bismuth salt into each of two test tubes and add 4-5 drops of hydrogen sulphide solution to both. Note the colour of the precipitate.

Add 3-4 drops of ammonium sulpnide to one test tube with the obtained bismuth sulphide. Compare the result with the result of the corresponding reaction of antimony sulphide precipitation.

Add 2-3 drops of concentrated nitric acid to the other test tube containing bismuth sulphide and observe dissolution of the precipitate. If dissolution is slow, heat the test tube slightly.

Recording the results. Describe your experiment. Write down the equations for the reactions by which bismuth sulphide is prepared. Compare the properties of antimony sulphide and bismuth sulphide as regards the action of excess ammonium sulphide. How can the different properties be explained? Write down the equation for bismuth sulphide dissolution in nitric acid, keeping in mind that bismuth(III) sulphate is formed in this reaction and that nitric acid is reduced to nitrogen oxide.

5. Reducing Properties of Antimony(III) and Bismuth(III) Compounds

A. Action of potassium permanganate on antimony(III) chloride and bismuth(III) nitrate

Procedure. Place 2-3 drops of potassium permanganate solution into each of two test tubes and add the same amount of 2 *N* hydrochloric acid to both. Add 3-5 drops of antimony chloride solution into one test tube and the same amount of bismuth nitrate solution to the other. Observe vanishing colour in the first test tube. Does analogous reaction occur in the other test tube?

Recording the results. Write down the equation for reduction of potassium permanganate to manganese(II) chloride and for oxidation of $SbCl_3$ to $H[SbCl_6]$. Note the different reducing properties of Sb^{3+} and Bi^{3+} ions.

B. Oxidation of bismuth(III) nitrate with bromine in an alkaline medium

Procedure. Place 1-2 drops of a bismuth(III) salt solution into a small crucible and add 3-5 drops of a 2 *N* alkali solution and 4-6 drops of bromine water. Place the crucible on an asbestos-centred gauze and heat over a small flame until a pale brown substance (mainly sodium metabismuthate, $NaBiO_3$) precipitates. Save the prepared $NaBiO_3$ for test 7 of the Experiment.

Recording the results. Write down the reaction equation. How does the oxidation state of bismuth change in the reaction? Write down the structural formula for sodium bismuthate. Can this salt be used as a reducing agent? Or as an oxidant? Explain your answer.

6. Reduction of Bismuth(III) Salt

Procedure. Place a drop of tin(II) chloride solution into a test tube and add 5-6 drops of 2 *N* sodium hydroxide solution to dissolve the tin(II) hydroxide that first precipitates. Add a drop of bismuth (III) salt solution to the obtained solution and observe rapid precipitation of black metallic bismuth.

Recording the results. Write down the reaction equation, considering that in an alkaline medium tin(IV) forms a complex anion $[Sn(OH)_6]^{2-}$ which gives the salt $Na_2[Sn(OH)_6]$ sodium hexahydroxystannate(IV). Indicate the oxidant and the reductant in this reaction.

7. Oxidizing Properties of Bismuth(V) Compounds

Procedure. Place 1-2 drops of manganese(II) sulphate into a conical test tube and add 2-3 drops of 2 *N* nitric acid and a microspatula of powdered sodium bismuthate prepared in test 5*B*. Note the violet colour characteristic of permanganate ion.

Recording the results. Write down the equation of the reaction, if sodium bismuthate converts into bismuth(III) nitrate, while manganese(II) sulphate into permanganic acid.

8. (Control Test)

Procedure. Obtain an unknown salt or its solution from the instructor. If this is a dry salt, dissolve it in water in a test tube by stirring the mixture using a glass rod. Pour the solution into two test tubes and use the known reactions to identify which salt, $Bi(NO_3)_3$ or $SbCl_3$, was given.

Recording the results. Write down the equations for the reactions and describe the observed phenomena which are used to make conclusions.

15 Elements of Subgroup IVA

QUESTIONS AND PROBLEMS

1. Write down the equations for the reactions by which carbon(II) oxide is prepared by three different methods. How can CO be separated from CO_2 by one of these methods?

2. Explain the formation of the triple bond in the CO molecule (a) by the valence bond method and (b) by the molecular orbital method. Draw the corresponding energy diagram. Indicate the number of bonding and anti-bonding orbitals. What is the multiplicity of the bond in the CO molecule?
3. What is the hybridization type of atomic orbitals of carbon during formation of the CO_2 molecule? What is the spatial configuration of the molecule? Draw a corresponding diagram.
4. A certain volume of a mixture of carbon monoxide and carbon dioxide was slowly passed at a high temperature through a tube containing excess amount of copper oxide. What happens to the copper oxide? Write down the reaction equation. Do the composition and the volume of the gaseous mixture change as the gas leaves the tube?
5. The molecules of what substance and what ions are present in an aqueous solution of carbon dioxide? Write down the equilibrium equation for this solution. How will the concentration of carbon dioxide change if alkali is added to the solution?
6. Why does calcium carbonate dissolve in water saturated with carbon dioxide? Write down the corresponding equation and explain the process of dissolution using the solubility product rule.
7. Is the pH of solutions of the alkali metal carbonates lower or higher than 7? Explain your answer and write down the corresponding reaction equations.
8. How will sodium carbonate react with calcium chloride, copper chloride, or aluminium chloride in an aqueous medium? Write down the equations for the reactions.
9. What is the spatial configuration of the methane molecule? How can the equivalence of all four bonds in the molecule be explained?
10. How can it be explained that methane, unlike HCl, has no acid properties and cannot form complex compounds?
11. A mixture of carbon monoxide, carbon dioxide, methane, and acetylene was passed successively through bromine water and sodium hydroxide solution. Write down the equations for the corresponding reactions. What is the composition of the remaining gaseous mixture?
12. Complete the following:

(a) $Si + HF + HNO_3 = NO + H_2SiF_6 + \ldots$
(b) $Si + NaOH + H_2O =$
(c) $SiO_2 + KOH =$
(d) $Mg_2Si + HCl =$
(e) $Mg_2Si + NH_4Cl = SiH_4 + NH_3 + \ldots$
(f) $SiO_2 + HF =$
(g) $Na_2SiO_3 + NH_4Cl + H_2O =$

13. How can (a) silicon, (b) silicon tetrafluoride, and (c) sodium silicate be prepared from quartz sand? Write down the equations for the corresponding reactions.
14. The chemical composition of orthoclase is expressed by the formula $K_2O \times \times Al_2O_3 \cdot 6SiO_2$. Write down the equation for erosion of orthoclase under the action of carbon dioxide and water.
15. What reaction occurs in an aqueous solution of sodium silicate? What happens when ammonium chloride is added? Write down the equations for the corresponding reactions. In which case is the reaction more complete? Explain your answer.
16. What reagent can simultaneously discover CO_3^{2-} and SiO_3^{2-} ions in a solution containing sodium carbonate and sodium silicate?
17. How do germanium, tin or lead react with hydrochloric acid, sulphuric acid and nitric acid (concentrated and dilute)? Write down the equations for

the corresponding reactions. In which of these reactions does lead almost completely dissolve?
18. How do (a) the reducing properties change in the series Ge^{2+}, Sn^{2+}, Pb^{2+}; (b) oxidizing properties change in the series Ge^{+IV}, Sn^{+IV}, Pb^{+IV}? Indicate the weakest reductant and the strongest oxidant. Draw electron structures of these elements in the corresponding oxidation state.
19. Which element of the germanium subgroup and in what oxidation state can form the hydroxide with (a) strongest basic properties; (b) strongest acidic properties? Write down the formulas of these hydroxides.
20. Write down the equations for the reactions illustrating the amphoteric properties of (a) tin(II) hydroxide, (b) lead(II) oxide.
21. In order to dissolve tin(II) chloride in water, hydrochloric acid and tin metal are added. What role do these substances play in the dissolution process? Write down the equations for the corresponding reactions.
22. Write down the equation for the reaction by which ammonium thiogermanate is prepared from the sulphides of germanium and ammonium, and for the interaction of ammonium thiogermanate with acid.
23. Write down the equations for the reactions by which tin(II) sulphide, tin(IV) sulphide and lead(II) sulphide are prepared from solutions of their salts. Which sulphide is soluble in ammonium sulphide? Which sulphide dissolves in ammonium disulphide? Write down the equations for the corresponding reactions.
24. How can the following conversions be accomplished:

(a) $Sn^{2+} \rightarrow [Sn(OH)_6]^{4-}$
(b) $Sn^{2+} \rightarrow [Sn(OH)_6]^{2-}$
(c) $[Pb(OH)_6]^{4-} \rightarrow Pb^{2+}$
(d) $Pb^{2+} \rightarrow PbO_2$
(e) $PbO_2 \rightarrow Pb^{2+}$
(f) $Sn^{2+} \rightarrow SnS_3^{2-}$
(g) $SnS^{2-} \rightarrow SnS_2$
(h) $GeS_2 \rightarrow GeS_3^{2-}$

Write down complete molecular equations for each reaction.

Examples of Multiple-choice Questions

1. Hydrochloric acid was added to the solutions of the following salts. In which reaction does a precipitate fall out?
(1) Na_2CO_3; (2) Na_2SiO_3; (3) $Sn(NO_3)_2$; (4) $Pb(NO_3)_2$; (5) $GeCl_2$.
2. Calculate the coefficient for sodium hydroxide in the reaction
$SnCl_2 + NaOH + Bi(NO_3)_3 \rightarrow Na_2[Sn(OH)_6] + Bi + NaNO_3 + NaCl$
(1) 6; (2) 12; (3) 18; (4) 24; (5) 4.
3. In which of the following reactions will SnS_2 precipitate?
(1) $SnCl_2 + Na_2S_2$ (excess); (2) $SnCl_2 + (NH_4)_2S$; (3) $(NH_4)_2SnS_3 + HCl$; (4) $SnCl_2 + H_2S$; (5) $(NH_4)_2SnS_3 + NaOH$ (excess).
4. Indicate the type of hybridization of the carbon atom orbitals in the CH_4 molecule, if the molecule is tetrahedral.
(1) *sp*; (2) sp^2; (3) sp^3; (4) sp^3d^2; (5) none.
5. Which of the following oxides has the strongest basic properties?
(1) SnO; (2) GeO; (3) GeO_2; (4) PbO_2; (5) PbO.

EXPERIMENT 33. CARBON

Apparatus and reagents

Dropping pipette.
Apparatus for preparing carbon monoxide and dioxide. Filtering paper.
Activated carbon. Charcoal, powder.
Fuchsine. Copper oxide. Marble.
Chalk.
Basic copper carbonate. Lime water.
Bromine. Litmus, neutral solution.
Formic acid.
Solutions: lead nitrate, 0.01 *N*; potassium iodide, 0.1 *N*; potassium permanganate, 0.05 *N*; silver nitrate, 0.1 *N*; sodium carbonate, 0.5 *N*; potassium carbonate, 0.5 *N*; potassium bicarbonate, 0.5 *N*; iron(III) chloride, 0.5 *N*; chromium chloride, 0.5 *N*; sulphuric acid, density 1.84 g/cm³; hydrochloric acid, density 1.19 g/cm³, 2 *N*; sodium hydroxide, 2 *N*; ammonia solution, 25%.

1. Adsorptive Properties of Carbon

A. Adsorption of pigment from a solution

Procedure. Half fill a test tube with a pale pink solution of fuchsine and add a small portion of activated carbon. Close the test tube with a finger tip and shake energetically for 2-3 minutes. Allow the solution to stand and observe its decolourization.

B. Adsorption of gas

Procedure. (*Use the hood*!) Carry out the experiment under supervision of the laboratory assistant. Fill a test tube with bromine gas. To do so, dip a glass rod into liquid bromine to a depth of 1 cm. Remove the glass rod and put it into the test tube carefully to touch the bottom. Remove the glass rod and add quickly a small portion of carbon powder. Close the test tube tightly and shake energetically several times. Observe decolourization of the gas in the test tube.

C. Adsorption of ions from a solution

Procedure. Place 2-3 drops of a 0.01 *N* lead nitrate solution into a test tube and add a drop of 0.1 *N* potassium iodine. Observe precipitation of lead iodide. (Keep the test tube with the precipitate as a reference.) Half fill another test tube with the same lead nitrate solution and add a small portion of activated carbon (3-4 microspatulas). Close the test tube with a finger tip and shake energetically for 2-3 minutes. Allow the mixture to stand and transfer 3-4 drops of the clear solution into another test tube using a pipette. Add a drop of

0.1 *N* solution of KI. Compare the amounts of lead iodide precipitates in the first and the second case. Explain the difference.

Recording the results. Describe your observations. Write down the reaction equations.

2. Reducing Properties of Carbon

A. Reduction of copper oxide with carbon

Procedure. Mix one volume of copper oxide powder with two volumes of carbon powder on a sheet of filter paper. Transfer the mixture into a cylindrical test tube and fix it in the stand in the horizontal position.

Heat the mixture over a strong flame for 10-12 minutes so that the mixture becomes red hot. Cool the test tube content and discharge it onto a sheet of white paper. Note the colour of the obtained product and the lustrous red coating on the test tube walls and explain its formation. Write down the reaction equation.

B. Reduction of sulphuric acid with carbon

Procedure. Place 2-3 drops of concentrated sulphuric acid (density 1.84 g/cm^3) into a microflask or a cylindrical test tube and add a small piece of coal. Fix the microflask in the stand and heat carefully over a small flame. Observe gas bubbling. Identify one of the liberated gases by its odour.

Recording the results. Write down the reaction equation, bearing in mind that carbon is oxidized to carbon dioxide. What substance has been reduced?

3. Preparing Carbon(II) Oxide and Its Burning

Procedure. (*Use the hood!*) Place 2-3 drops of concentrated sulphuric acid (density 1.84 g/cm^3) into a microflask and add 4-5 drops of formic acid HCOOH. Close the flask with a stopper provided with a straight gas-discharge tube. Fix the flask in the stand in the vertical position (see Fig. 22*e*). Heat the mixture over a low flame of the burner and light the evolving gas. *Be careful, since a mixture of CO with air is explosive!* Note the colour of the flame.

Write down the equation for the reaction by which carbon monoxide is produced and for the reaction of its burning.

4. Reducing Properties of Carbon Monoxide

(Use the hood to carry out tests 4*A* and 4*B*.)

A. Reduction of silver

Procedure. Prepare a solution of $[Ag(NH_3)_2]OH$. For this purpose, place 3 drops of silver nitrate solution into a test tube and add 1-2 drops of 2 *N* sodium hydroxide solution. Dissolve the silver oxide precipitate in a drop of a 25% solution of ammonia.

Prepare carbon monoxide as instructed in the previous test 3. Fix a microflask with the reaction mixture in the stand, close the flask with a stopper fitted with a bent gas-discharge tube, and lower its end in a test tube containing the complex silver compound (see Fig. 22*d*). Heat the reaction mixture slightly and pass the evolving gas into the solution until colloidal silver precipitates.

Recording the results. Write down the equations for the reactions by which (a) silver oxide is prepared by the interaction between silver nitrate and sodium hydroxide; (b) the silver complex compound is formed by the reaction of silver oxide and ammonia; (c) silver is reduced from its complex compound with carbon monoxide according to the following equation:

$$2[Ag(NH_3)_2]OH + CO = 2Ag + 4NH_3 + H_2O + CO_2$$

B. Reduction of potassium dichromate

Procedure. Place 2-3 drops of $K_2Cr_2O_7$ solution into a test tube and add 1-2 drops of 2 *N* sulphuric acid and a drop of $Hg(NO_3)_2$ solution as a catalyst. Pass CO into the prepared solution till the colour changes. Write down the equation for the reaction by which potassium dichromate is reduced to chromium(III) sulphate. To what compound has carbon monoxide been oxidized?

5. Preparing Carbon Dioxide and Its Dissolution in Water

Procedure. Place 5-6 drops of neutral litmus solution into a test tube. Place 3-4 small pieces of marble into a microflask and fix it in the stand in the vertical position. Add 5 drops of water and 10 drops of concentrated hydrochloric acid. Close the flask quickly with a stopper containing a gas-discharge tube. Lower the tube end into the test tube containing litmus solution and pass the evolving gas for 2-3 minutes (See Fig. 22*d*). Observe the colour change of litmus.

Recording the results. Describe your experiment. Write down the equation for the equilibrium in the aqueous solution of carbon dioxide. How will the equilibrium be shifted if alkali or acid is added? Indicate the cause of the shift in the equilibrium in each case.

6. Sparingly Soluble Carbonates of Certain Metals

A. Preparing carbonates of alkaline-earth metals and their dissolution in acetic acid

Procedure. Prepare carbonates of calcium, strontium and barium in three separate test tubes by the reaction of the corresponding salts with sodium carbonate (taking 3-4 drops of each salt). Allow the solutions to settle, remove part of liquid using a pipette or filter paper and add a drop of acetic acid into each test tube. What happens?

Recording the results. Observe precipitation and note the colour of the precipitates which dissolve in acetic acid with evolution of gas. Write down the equations for all reactions.

B. Formation of hydroxocarbonates of certain metals

Procedure. Place 3-4 drops of solutions of magnesium, cobalt and cadmium salts into three separate test tubes and add equal volumes of sodium carbonate solution to each salt.

Recording the results. Observe precipitation of hydroxocarbonates of said metals, and note their colour. Observe evolution of gas bubbles. Write down the ionic and molecular equations for the reactions in which water is also involved.

7. Hydrolysis of Sodium Carbonate and Hydrocarbonate

Procedure. Place 3-4 drops of neutral litmus solution into each of two test tubes and add 1-2 drops of sodium carbonate into one and of sodium hydrocarbonate into the other test tube. Note the different colour of litmus in the test tubes.

Recording the results. Write down the ionic and molecular equations for the hydrolysis of sodium carbonate and sodium hydrocarbonate. In which case is the hydrolysis weaker? Explain.

8. Effect of CO_3^{2-} Ion on Hydrolysis of Certain Salts

Procedure. Place 3-4 drops of iron(III) salt into one test tube and the same amount of stannous salt into the other test tube and add 3-5 drops of sodium carbonate to each solution.

Recording the results. Observe liberation of gas and precipitation of the hydroxides of iron and tin. Write down the equations for the hydrolysis of said salts when sodium carbonate is added to them. Why does the hydrolysis of the salts proceed practically to the end in the presence of CO_3^{2-} ion?

9. Thermal Decomposition of Carbonates

Procedure. Place small amount (about 1/8 test tube) of dry copper hydrocarbonate into one test tube and of calcium carbonate (chalk powder) into the other test tube. Fix the test tube containing the copper salt in the stand in an inclined position with the tube mouth down. Close the test tube with a stopper provided with a bent gas-discharge tube. Lower the tube end into a test tube filled with lime water (see Fig. 42). Heat the test tube containing the salt over a low flame of the burner. What happens to lime water? Explain your observations. What is the composition of the precipitate? Write down the equation for the thermal decomposition of copper hydroxocarbonate and for the reaction between the evolving gas and lime water.

Act similarly with the calcium salt. Heat $CaCO_3$ more energetically and for a longer time. Observe the reaction. Note the different thermal stability of the salts. Write down the reaction equations.

EXPERIMENT 34. SILICON

Apparatus and reagents

Crucible. Clay triangle. Asbestos-centred gauze. Forceps. Filter paper. Glass rods. Cylindrical test tubes. Porcelain mortar with a pestle. Micropipettes. Sodium hydroxide, dry. Magnesium powder. Silica gel, calcined. Quartz sand. Solutions: hydrochloric acid, 4 *N*, 2 *N*, density 1.19 g/cm³; sodium silicate, 2 *N*, saturated; sodium hydroxide, 2 *N*; calcium chloride, 0.5 *N*; cobalt nitrate, 0.5 *N*; lead nitrate, 0.5 *N*; copper sulphate, 0.5 *N*; ammonium chloride, 0.5 *N*; sodium hydroxide, 2 *N*; ammonia solution, 25%, tetramminecopper sulphate.

Prepare silica gel as follows: mix equal volumes (50 ml) of soluble glass and hydrochloric acid (37%, density 1.19 g/cm³). Allow the mixture to stand for 24 hours. Cut the formed gel into pieces and wash in a beaker by decantation until chloride ions are removed completely (test with $AgNO_3$). Dry the washed gel at a temperature of 40-50°C for 24 hours and then at 50-100°C for 10-12 hours.

1. Preparing Magnesium Silicide, Silane, and Silicon

Procedure. Place 3 microspatulas of silicon dioxide (quartz sand or silica gel) on a sheet of paper, add 4-5 microspatulas of magnesium powder, mix thoroughly, using a glass rod, and transfer the mixture into a cylindrical test tube. Fix the test tube in the stand and heat first the entire test tube and then only that part where the mixture is. As soon as the mixture becomes strongly heated, move the burner aside. Cool the test tube, transfer it into a porcelain mortar, break with a pestle, and separate the sintered mass from glass. Place 10-15 drops of 4 *N* hydrochloric acid in a crucible and add small pieces of the sintered mass. The sintered mass consists of silicon, magnesium oxide, and magnesium silicide. Observe self-ignition of the evolving silane SiH_4 and formation of a white smoke of SiO_2; note the colour of silicon powder that remains on the crucible bottom. What reagent can dissolve it? Write down the reaction equations.

Recording the results. Write down the equations for the following reactions: (a) reduction of silicon dioxide with magnesium to form magnesium silicide; (b) interaction of magnesium silicide with hydrochloric acid; (c) burning of silane.

2. Preparing Gel and Sol of Silicic Acid

Procedure. Place 4-5 drops of sodium silicate into one test tube and the same amount of concentrated hydrochloric acid (density 1.19 g/cm^3) into another test tube. Add 6-7 drops of 2 *N* hydrochloric acid to the first test tube and 1-2 drops of saturated sodium silicate solution into the other test tube. Close the test tubes with the finger tip and shake. Observe the formation of silicic acid gel in the first test tube and the sol of silicic acid in the other test tube. Heat the obtained sol over a small flame until it turns into a gel. What is the name of the process by which a sol is converted into a gel? What is the role of heating in this conversion?

Recording the results. Describe the experiment. Write down the equation for the reaction by which silicic acid H_2SiO_3 is formed. (The formula is only conventional because the composition of silicic acids is more complicated and can be expressed by the general formula $SiO_2 \cdot xH_2O$.)

3. Adsorbing Properties of Silica Gel

Procedure. Place 5-7 drops of tetramminecopper sulphate solution into a test tube and add crushed silica gel. Close the test tube with a finger tip and shake energetically. Observe colouration of silica gel and fading the solution colour due to adsorption of $[Cu(NH_3)_4]^{2+}$

ions by silica gel. Allow the solution to settle, pour off the supernatant liquid (or remove it using a pipette). Wash the remaining silica gel with distilled water 2-3 times. Add 5-10 drops of hydrochloric acid and observe decolourization of silica gel due to destruction of the coloured ions by hydrochloric acid according to the equation:

$$[Cu(NH_3)_4]^{2+} + 4H^+ = Cu^{2+} + 4NH_4^+$$

4. Salts of Silicic Acid

A. Preparing sodium silicate (soluble glass)

Procedure. Place a crucible on a clay triangle and, using forceps, place a grain of sodium hydroxide (the size of a pea) into it. Heat the crucible to melt the alkali. Add a microspatula of calcined silica gel into the melt and heat the mixture again to melt it completely. Carry out the following experiment to prove that the reaction products is a silicate. Cool the crucible, add 5-8 drops of distilled water and stir thoroughly using a glass rod. Using a pipette, transfer a few drops of the solution into a cylindrical test tube. Add an equal volume of 2 *N* hydrochloric acid and heat over a low flame of the burner. Note the formation of silica gel. Write down the equations of the reactions by which sodium silicate and silicic acid (with the conventional formula H_2SiO_3) are obtained.

B. Preparing sparingly soluble silicates

Procedure. Place 3-5 drops of calcium chloride solution into one test tube, the same amount of cobalt nitrate into another test tube, the same amount of lead nitrate into the third, and of copper sulphate solution into the fourth test tube. Add 2-3 drops of sodium silicate to each test tube. Note the colour of the precipitates.

Write down the equations of the reactions.

5. Hydrolysis of Sodium Silicate

Procedure. Place 5-6 drops of sodium silicate solution into each of two test tubes and add a drop of phenolphthalein into one of them. Observe red colouration. The colour indicates an excess of which ion? Add 4-5 drops of ammonium chloride into the other test tube.

Recording the results. Describe your observations and explain the different degree of hydrolysis of sodium silicate in water and in the presence of ammonium chloride. Write down the ionic and molecular equations for both cases of hydrolysis. Which ion increases the degree of hydrolysis in the second case? How can hydrolysis of sodium silicate be decreased?

EXPERIMENT 35. GERMANIUM. TIN

Apparatus and reagents

Water bath. Lance. Beaker, 10-15 cm high.
Capillary pipette.
Micropipette. Carbon powder. Carbon black. Germanium dioxide. Germanium tetrachloride. Tin, granules. Zinc, granules. Tin oxide. Tin(II) chloride. Hydrogen sulphide solution. Solutions: hydrochloric acid, 2 *N*, 6 *N*, density 1.19 g/cm^3; sulphuric acid, 2 *N*, density 1.84 g/cm^3; nitric acid, 2 *N*, density 1.4 g/cm^3; sodium hydroxide, 2 *N*, 10%, 40%; tin(II) chloride, 0.5 *N*; tin(IV) chloride, 0.5*N*; potassium dichromate, 0.5 *N*; potassium permanganate, 0.5 *N*; ammonium sulphide, 0.5 *N*; ammonium polysulphide, 0.5 *N*.
Prepare a saturated solution of germanium dioxide as follows: mix 5 g of germanium dioxide in an Erlenmeyer flask with 200 ml of distilled water. Stir the solution and allow it to settle. Then filter the solution using a double filter (a blue strip). The filtration is very slow. Prepare hexachlorogermanic acid as follows: dissolve 5 g of germanium dioxide in 50 ml of a 10% solution of sodium hydroxide and add 2 *N* hydrochloric acid to an obviously acidic reaction (litmus paper). Dilute with distilled water to make 500 ml.

1. Reduction of Germanium Dioxide

Procedure. Mix equal volumes of germanium dioxide powder and carbon black in porcelain mortar. Transfer a portion of the mixture into a test tube and heat. Observe deposition of a brown germanium on the test tube walls. Write down the reaction equation.

2. Reduction of Hexachlorogermanic Acid

Procedure. Place equal volumes of hexachlorogermanic acid and 2 *N* sulphuric acid into a test tube and add a granule of zinc. Observe precipitation of germanium on the zinc (a light brown deposit). By what mechanism is germanium replaced from its complex compound by zinc? Write down the reaction equation.

3. Hydrolysis of Germanium Salt

Procedure. Dissolve crystalline germanium tetrachloride in about the same volume of water. After complete dissolution of the salt, add 3-4 drops of water in excess and observe the formation of the gel $GeO_2 \cdot nH_2O$ due to hydrolysis of the salt. The addition of what salt can slow down the hydrolysis? Prove your answer experimentally. Write down the reaction equation.

4. Preparing Germanium Disulphide

Procedure. Place equal volumes of a saturated solution of germanium dioxide and 6 *N* hydrochloric acid in a test tube. Stir the mixture using a glass rod and add ammonium sulphide solution to precipitate germanium sulphide. Note the colour of the sulphide and write down the reaction equation.

5. Reduction of Tin Oxide with Carbon

Procedure. Place 2-3 microspatulas of tin(II) oxide on a sheet of paper, add two volumes of carbon powder and mix. Transfer the mixture into a cylindrical test tube and fix it in the stand in the horizontal position. Heat the mixture over a burner for 10 minutes. Cool the test tube and transfer its contents onto a sheet of paper. Regard the reaction product (tin).

Write down the equation of the reaction by which tin(II) oxide is reduced with carbon.

6. Reduction of Tin(II) from Solution

Procedure. Place 5-6 drops of tin(II) chloride solution into a test tube and add a small grain of zinc: observe precipitation of metallic tin on the zinc surface.

Write down the ionic equation for the reaction.

7. Reaction of Tin with Acids

A. Action of dilute acids on tin

Procedure. Place a small piece of tin metal into each of three test tubes and add 4-6 drops of 2 *N* solutions of hydrochloric acid, sulphuric acid and nitric acid separately into test tubes. Observe the slow reaction in the cold. Heat the test tubes on a water bath or over a low flame of a burner (*Caution*!). Observe liberation of gas.

Recording the results. Write down the equations for the reactions observed, taking into account that tin reacts with dilute nitric acid to liberate mainly NO, while tin is oxidized to Sn^{2+} in all test tubes to give the corresponding salts. What gas liberates in the second test tube during the interaction of tin with dilute sulphuric acid and in the first test tube where hydrochloric acid was added?

B. Action of concentrated acids on tin

Procedure. Discard the dilute acids carefully, wash tin with water, and add 4-5 drops of concentrated hydrochloric acid (density 1.19 g/cm^3) into the first test tube, sulphuric acid (density 1.84 g/cm^3)

into the second test tube, and nitric acid (density 1.4 g/cm^3) into the third test tube. How do the reactions proceed without heating? Now heat the test tubes in a water bath or over a low flame of the burner. (*Caution!*) Observe the reaction with heating. What gas liberates in the first test tube? Identify the gas evolving in the second test tube by its odour.

Recording the results. Write down the equations for the reactions. It is known that when tin reacts with concentrated sulphuric acid, it is oxidized to Sn^{IV} and $Sn(SO_4)_2$ forms, while sulphuric acid is reduced to SO_2. Tin reacts with concentrated nitric acid to give a white precipitate of beta-stannic acid of the complicated composition $xSnO_2 \cdot yH_2O$, which is conventionally assigned the formula H_2SnO_3 (metastannic acid). Concentrated nitric acid is reduced in this reaction mainly to NO_2.

8. Tin(II) Hydroxide and Its Properties

Procedure. Place 2-4 drops of tin(II) chloride into each of two test tubes. Add 2-5 drops of 2 *N* sodium hydroxide solution into both test tubes until a precipitate falls out. (Avoid adding excess alkali.) Add 3-5 drops of 2 *N* hydrochloric acid to the first test tube and the same amount of 2 *N* sodium hydroxide solution to the second test tube. Stir the solutions using a glass rod or shaking carefully to dissolve the formed precipitates.

Recording the results. Describe your observations and the properties of tin(II) hydroxide. Write down the equations for the reactions by which tin(II) hydroxide is prepared and by which it reacts with alkali and acid, taking into account that the complex anion $[Sn(OH)_4]^{2-}$ (tetrahydroxystannate) is formed in the alkaline solution. Which ions of tin are mainly present in solution at pH below and above 7?

9. Hydrolysis of Tin(II) Chloride

Procedure. Place 1-4 drops of water into a test tube and add 2-3 crystals of tin(II) chloride. Stir the contents using a glass rod to dissolve the crystals completely. Add 5-6 drops of water to the obtained clear solution. Observe precipitation of the basic salt of tin(II) SnOHCl. The addition of what reagent can decrease hydrolysis of tin(II) chloride? Prove your answer experimentally. Observe the reaction.

Recording the results. Write down the equations for all reactions observed. Explain how the addition of water or acid influences the degree of hydrolysis of this salt.

10. Reducing Properties of Tin(II) Compounds

A. Reduction of potassium permanganate with tin(II) chloride

Procedure. Add 1-2 drops of 2 *N* hydrochloric acid and 3-4 drops of a tin(II) salt into a test tube containing 3-5 drops of potassium permanganate. Observe the reaction. Write down the equation for the reaction occurring with formation of manganese(II) chloride. To which oxidation state has tin been converted?

B. Reduction of potassium dichromate

Procedure. Place tin(II) chloride solution into a test tube and add 1-3 drops of hydrochloric acid. Then add, drop by drop, 2 or 3 drops of potassium dichromate solution. Observe the appearance of green colour due to reduction of $Cr_2O_7^{2-}$ ion to Cr^{3+} ion. Write down the reaction equation.

C. Reduction of iron(III) chloride

Procedure. Place 1-2 drops of iron(III) chloride solution into one test tube and the same amount of potassium ferricyanide $K_3[Fe(CN)_6]$ (the reagent for Fe^{2+}) into the second. Add water to both test tubes. Note the colour of the resultant solutions. Save one test tube as reference, and add 2-3 drops of tin(II) chloride solution to the other. Observe blue colour due to the formation of iron(II) hexacyanoferrate $Fe_3[Fe(CN)_6]_2$. Explain why the solution in the first test tube does not colour blue.

Write down the equation for the oxidation-reduction reaction and for the reaction by which iron(II) hexacyanoferrate(III) is formed.

11. Tin(II) Sulphide and Its Properties

Procedure. Place 2-3 drops of tin(II) chloride solution into each of two test tubes and add 5-6 drops of freshly prepared hydrogen sulphide solution to both. Observe precipitation of tin(II) sulphide and note its colour. Allow the solutions to settle and remove the supernatant from the test tubes using a strip of filter paper. Add 3-4 drops of freshly prepared ammonium sulphide solution to the precipitate in the first test tube and the same amount of ammonium disulphide $(NH_4)_2S_2$ to the precipitate in the other. Shake the test tubes several times energetically or stir the solutions using a glass rod. In which test tube does the precipitate dissolve?

Recording the results. Write down the equations for the reactions (a) by which tin(II) sulphide is prepared; (b) by which tin(II) sulphide reacts with ammonium disulphide in two stages, keeping in mind that tin(II) sulphide is oxidized by ammonium disulphide to SnS_2 which is then dissolved in ammonium sulphide to give ammonium thiostannate $(NH_4)_2SnS_3$.

Note and explain the different properties of the sulphides of tin(II) and tin(IV).

12. Tin(IV) Hydroxide and Its Properties

Procedure. Place 2-4 drops of tin(IV) chloride solution into each of two test tubes and add 2-4 drops of 2 *N* sodium hydroxide solution to both test tubes until a precipitate falls out. Add a few drops of hydrochloric acid to the precipitate in one test tube and a few drops of sodium hydroxide solution into the other test tube (to dissolve the precipitates in both tubes).

Recording the results. Write down the reaction equations of tin(IV) hydroxide formation and its dissolution in acid and alkali, bearing in mind that the complex ion of tin(IV) $[Sn(OH)_6]^{2-}$ is formed in an alkaline medium. What are the properties of tin(IV) hydroxide? How does the concentration of the Sn^{4+} and $[Sn(OH)_6]^{2-}$ ions change when alkali or acid is added? It should be noted that $[SnCl_6]^{2-}$ ion is formed in a strongly acidic medium in a great excess of acid.

13. Tin(IV) Sulphide and Its Properties

A. Preparing tin(IV) sulphide

Procedure. Place 1-2 drops of tin(IV) chloride solution into a test tube and add freshly prepared hydrogen sulphide solution. Note the colour of the precipitate and write down the equations of the corresponding reaction. (Save the precipitate for the next test *B*.)

B. Preparing thiostannate

Procedure. Allow the precipitate prepared in the previous test *A* to settle, remove excess liquid using filter paper, and add 5-6 drops of ammonium sulphide. Close the test tube with a finger tip and shake energetically so that tin disulphide dissolves completely to form ammonium thiostannate $(NH_4)_2SnS_3$. Does tin(II) sulphide dissolve in ammonium sulphide? Write down the equation for the corresponding reaction.

C. Destruction of ammonium thiostannate in acidic medium

Procedure. Add 2-3 drops of concentrated hydrochloric acid to the thiosalt of tin obtained in the previous test *B*, and observe precipitation. What substance precipitates? What gas is liberated?

Recording the results. Describe the observed phenomena.

Write down the ionic and molecular equations for the reaction between ammonium thiostannate and hydrochloric acid. In which medium are the thiosalts stable, at pH below or above 7? How can the difference in the properties of the sulphides SnS and SnS_2 be explained?

EXPERIMENT 36. LEAD

Apparatus and reagents

Asbestos-centred gauze.
Crucible. Forceps. Lance or blade. Hammer. Blowpipe. Beaker, 10-15 cm high. Cast-iron plate. Capillary pipette.
Coal, lump, at least 5 × 5 cm. Zinc, granules. Lead(II) oxide. Lead. Lead dioxide. Minium. Solder.
Starch-iodine paper. Starch solution.
Solutions: hydrogen sulphide solution; hydrochloric acid, 4 *N*, 2 *N*, density 1.19 g/cm³; nitric acid, 2 *N*, density 1.4 g/cm³; sulphuric acid, 2 *N*, density 1.84 g/cm³; sodium hydroxide, 2 *N*, 40%;
lead nitrate or acetate, 0.5 *N*;
potassium iodide, 0.1 *N*;
hydrogen peroxide, 3%;
sodium carbonate, 0.5 *N*;
sodium sulphate 0.5 *N*;
manganese sulphate, 0.5 *N*, chromium sulphate, 0.5 *N*.

1. Reduction of Lead(II) Compounds

A. Reduction of lead oxide with carbon

Procedure. Make a small pit in a lump of coal. Mix equal volumes of carbon and lead oxide (3-4 microspatulas each) on a sheet of paper and place the mixture into the pit in the coal.

Put the end of the blowpipe into the reducing flame of a gas burner (into the outer zone of the luminous flame) and blow slightly so that the flame of the burner is directed to the mixture of the coal and lead oxide. Heat the mixture until a drop of molten lead appears. Allow the melt to cool, remove it from the coal lump and try for ductility. To do so, put the lead on an iron or cast-iron plate and flatten with a hammer.

Recording the results. Describe the experiment. Write down the equation for the reaction by which lead is reduced from its oxide with carbon.

B. Reducing Pb^{2+} ion in a solution

Procedure. Place a piece of zinc into a test tube and add 5-6 drops of lead nitrate or acetate. Observe the appearance of lustrous crystals of lead.

Recording the results. Write down the ionic equation for the reaction. What metals can be used instead of zinc in this experiment?

2. Reaction of Lead with Acids

A. Action of dilute acids on lead

Procedure. Place one grain of lead into each of three test tubes and add 5-8 drops of 2 *N* acids: hydrochloric acid into the first test tube, sulphuric into the second, and nitric into the third test tube. Heat the test tubes over a small flame. Does the reaction occur in all test tubes? Cool the reaction mixtures and add 2-3 drops of potassium iodide solution into each test tube. In which test tube does lead iodide precipitate? In which acid does lead dissolve completely? Characterize the solubility of lead in the acids. Explain the different reaction of lead to the indicated acids.

Recording the results. Answer the questions. Write down the equations for the reactions, taking into account the fact that NO is predominantly liberated in the reaction between lead and nitric acid.

B. Action of concentrated acids on lead

Procedure. Discard carefully the solutions of acids from the test tubes, rinse lead with water, and try it with the following concentrated acids: hydrochloric (density 1.19 g/cm^3), sulphuric (density 1.84 g/cm^3), and nitric acid (density 1.4 g/cm^3). Add 3-5 drops of the acids. Observe the reaction in the cold. Then heat the test tubes in a water bath or over a low flame of the burner. (*Caution*!) Observe the reaction.

Cool the test tubes, add 2-4 drops of water and 2-3 drops of potassium iodide to each test tube and characterize solubility of lead in concentrated acids.

Recording the results. Note the formation of NO_2 in the reaction between lead and concentrated nitric acid, and of SO_2 in the reaction between lead and concentrated sulphuric acid. Write down the equations for the corresponding reactions, keeping in mind that lead is oxidized in all cases to Pb^{II} and reacts with sulphuric acid to give $Pb(HSO_4)_2$. What compound is produced in the reaction between lead and nitric acid? Does the concentration of hydrochloric acid influence the nature of reaction with lead?

3. Lead(II) Hydroxide and Its Properties

Procedure. Place 2-3 drops of a lead salt into each of two test tubes and add a few drops of 2 *N* sodium hydroxide solution into each test tube until a precipitate falls out. Study the properties of the obtained lead hydroxide by adding a few drops of 2 *N* nitric acid solution to one test tube and of 2 *N* sodium hydroxide solution to the other test tube. Stir the solutions using a glass rod or by shaking the test tubes carefully to dissolve the precipitates completely.

Recording the results. Describe the properties of lead hydroxide. Write down the equations for the reactions of lead hydroxide formation, its dissociation and dissolution in the acid and alkali, taking into consideration that the complex anion $Pb[(OH)_6]^{4-}$ (hexahydroxyplumbate) is formed in the alkaline medium. Why is nitric acid, rather than hydrochloric or sulphuric, used in this experiment?

4. Sparingly Soluble Lead(II) Salts

Procedure. Place 2-4 drops of the following 2 *N* solutions: sulphuric acid into the first test tube, hydrochloric acid into the second, potassium iodide into the third test tube and hydrogen sulphide solution into the fourth one. Add 2-3 drops of a lead salt solution into each test tube. Observe precipitation and note the colour of the precipitates. Add 2-3 drops of water to all four test tubes and heat in a water bath. Observe dissolution of lead chloride and lead iodide with heating. Put the test tubes into cold water in a beaker and observe precipitation of lead chloride and lead iodide on cooling. Do lead sulphate and lead sulphide dissolve with heating? Write down the equations for the reactions observed.

5. Hydrolysis of Lead(II) Salts

Procedure. Place 2-3 crystals of lead nitrate into a test tube and add 4-5 drops of water. Stir the contents using a glass rod to dissolve the crystals, and dip a blue litmus paper into the solution. Observe the reaction. What is the medium of the lead nitrate solution? Heat the solution slightly and add an equal volume of sodium carbonate solution. Heat again and observe precipitation of $2PbCO_3 \cdot Pb(OH)_2$. In which acid can this salt be dissolved? Prove your answer experimentally.

Recording the results. Explain your observations. Write down the equation for hydrolysis of lead nitrate (the first step of hydrolysis). What effect does the addition of sodium carbonate produce on hydrolysis? Write down the equation for the reaction of joint hydrolysis of lead nitrate and sodium carbonate.

6. Oxidation of Lead(II) Compounds with Hydrogen Peroxide

Procedure. Place 2-3 drops of a lead(II) salt in a test tube and add 2-3 drops of a 40% solution of sodium hydroxide and 4-6 drops of hydrogen peroxide solution. Stir the obtained solution of $Na_4[Pb(OH)_6]$ using a glass rod and heat in a water bath or over a low flame of the burner. Observe precipitation of brown lead dioxide. Allow the solution to settle, remove excess liquid using a pipette or filter paper, and wash the precipitate with 2-3 drops of water with stirring the mixture by a glass rod. Remove water using filter paper and save the precipitate for test 8*A*.

Recording the results. Write down the equations for the reactions (a) between lead nitrate and excess sodium hydroxide; (b) oxidation of $Na_4[Pb(OH)_6]$ with hydrogen peroxide. Can Pb^{II} be oxidized with potassium dichromate? (See Appendix, Table 11). Which oxidation state is more characteristic for lead: +II or +IV?

7. Amphoteric Properties of Lead Dioxide

A. Reaction of lead dioxide with hydrochloric acid

Procedure. Place 2-3 microspatulas of lead dioxide into a test tube and add a few drops of concentrated hydrochloric acid. Heat the test tube slightly in a water bath. Observe the yellow colour characteristic of lead tetrachloride. Note the basic properties of lead dioxide that are manifested in this reaction. Identify the evolving chlorine by odour (*caution*!) and by the blue colour of the starch-iodine paper.

Recording the results. Write down the equation for the reaction between lead dioxide and hydrochloric acid and for decomposition of lead tetrachloride. Note the instability of the compound.

B. Reaction of lead dioxide with alkali

Procedure. Place a microspatula of lead dioxide into a crucible and add 10-15 drops of a 40% solution of sodium hydroxide. Place the crucible on an asbestos-centred gauze and heat over a low flame with stirring the mixture using a glass rod for 2-3 minutes. Cool the crucible and transfer its contents into a test tube. Allow the precipitate to settle. Using a pipette, transfer 5-6 drops of the supernatant into a clean test tube. Which lead ion is present in the solution? Add a few drops of concentrated hydrochloric acid (density 1.19 g/cm^3) and observe the yellow colour of lead tetrachloride.

Recording the results. Describe your experiment and observations.

Write down the equations for the reaction between lead dioxide and sodium hydroxide to form $Na_2[Pb(OH)_6]$ taking into account

that water is involved in the reaction. What properties of lead dioxide are demonstrated in the reaction? Write down the reactions of sodium hexahydroxyplumbate(IV) with hydrochloric acid and of decomposition of lead tetrachloride.

Which reactions indicate the amphoteric properties of lead dioxide?

8. Oxidizing Properties of Lead Dioxide

A. Oxidation of chromium(III) sulphate

Procedure. Add 10 drops of a 40% solution of sodium hydroxide to the lead dioxide precipitate prepared in test 6 and heat the test tube in a water bath or over a low flame of the burner. Add one drop of chromium sulphate to a hot solution and heat the test tube again. Observe the appearance of yellow colour characteristic of CrO_4^{2-} ion.

Recording the results. Write down the equation for the reaction taking into account that lead(II) sulphate and chromate are sparingly soluble in water but are soluble in alkali and form hexahydroxyplumbates(II).

B. Oxidation of potassium iodide

Procedure. Place a microspatula of lead dioxide powder into a test tube and add 3-5 drops of 2 *N* sulphuric acid and 5-6 drops of potassium iodide solution. Heat the test tube over a low flame of a burner or in a water bath. Observe the colour change. Using a glass rod, transfer a drop of the solution into a test tube containing 8-10 drops of starch solution. Observe the development of blue colour.

Recording the results. Write down the equation for the reaction between lead dioxide and potassium iodide in an acidic medium.

C. Oxidation of manganese(II) sulphate

Procedure. Place a very small amount (at the tip of a microspatula) of lead dioxide into a test tube, add 6-8 drops of 2 *N* nitric acid solution and a drop of a manganese(II) salt, and boil carefully. If there is an excess lead dioxide, allow the solution to stand. Note the colour of the obtained solution.

Recording the results. Write down the equation for the reaction, keeping in mind that permanganic acid and a lead(II) salt are formed in the reaction.

9. Determining Oxidation State of Lead in Pb_3O_4

Procedure. Place a microspatula of powdered Pb_3O_4 into a test tube and add 5-6 drops of 2 *N* nitric acid. Heat over a low flame and ob serve the change in the colour of the precipitate. What substance is produced in the reaction? What is the oxidation state of lead in this compound? Allow the mixture to stand and transfer a few drops of the supernatant into a clean test tube. Add sodium sulphate solution and observe precipitation of a white substance. The presence of which ion is demonstrated by the precipitation? What is the precipitate?

Recording the results. Write down the equation for the reaction of Pb_3O_4 with nitric acid and for the reaction between the obtained lead compound and sodium sulphate. Express the formula of Pb_3O_4 as a combination of two oxides of lead in the corresponding oxidation states.

10. (Control Test)

Identification of tin and lead in solder

Tin and lead preserve their specific chemical properties in solder. Therefore, in order to convert the metals into their ions, the alloy should be treated with the corresponding acids. To do so, place a small grain of a solder into a test tube and add 5-8 drops of concentrated nitric acid (density 1.4 g/cm^3). Heat the test tube carefully until a precipitate falls out. Write down the reaction equation.

Add 5-8 drops of distilled water to the test tube, stir thoroughly using a glass rod, and allow the mixture to settle. What substance precipitates? Transfer the solution into a clean test tube and detect lead(II) ion using the reactions described above.

Place a granule of the solder into another test tube and add 5-8 drops of concentrated hydrochloric acid. Heat carefully and observe incomplete dissolution of the alloy in hot concentrated hydrochloric acid. What are the reaction products? Write down the equations for the reactions.

Cool the mixture, and transfer part of the solution into a clean test tube using a pipette. Which ions of tin are present in the solution? Establish the presence of tin(II) ions in the solution by its reducing properties. Can lead interfere with the detection of tin by these reactions? Explain your answer.

EXPERIMENT 37. SYNTHESIS OF LEAD DIOXIDE

Apparatus and reagents

Chemical balance.
Filter paper. Paper filters.
Glass funnel. Büchner funnel. Bunsen flask. Porcelain mortar with a pestle.
Beakers, 100-ml. Stand with a ring.

Asbestos-centred gauze. Drying cabinet.	Lead acetate. Bleaching powder (calcium hypochloride). Nitric acid, 0.2 *N*.

Procedure. Weigh out 3 g of lead acetate and dissolve in 20 ml of 2 *N* acetic acid solution. Calculate the amount of bleaching powder required for the reaction

$$Pb(CH_3COO)_2 + CaOCl_2 + H_2O = PbO_2 + CaCl_2 + 2HCH_3COO$$

Weigh out twice the calculated amount and dissolve it to prepare a saturated solution. To do so, triturate thoroughly bleaching powder in a mortar with 5 ml of water, then add another 10 ml of water, mix thoroughly and filter the mixture into a beaker. Heat lead acetate solution to 50°C with stirring and add it to the calcium hypochloride solution. Boil the mixture for 10-15 minutes until a precipitate falls out. Cool the mixture, separate the precipitated lead dioxide by filtration, and wash it with water two times on a Büchner funnel. Transfer the salt with the filter into a drying cabinet and dry at 100°C. Weigh the obtained lead dioxide and calculate the yield (in %) with respect to lead acetate. Handle the salt over to the instructor. Describe your work in the log-book.

16 Elements of Subgroup IIIA

QUESTIONS AND PROBLEMS

1. Write down the equations for the reactions by which (a) boron is prepared from boric acid, and (b) aluminium is obtained from Al_2O_3.
2. The first, second and third ionization potentials of aluminium are considerably lower than the corresponding ionization potentials of boron. How does this influence the ionic character of the bond in the molecules of Al_2O_3 and B_2O_3?
3. Write down the equation for the reaction between boron and concentrated nitric acid, bearing in mind that boric acid is produced by this reaction.
4. What substances are obtained by gradually calcining orthoboric acid? Write down the equations for the corresponding reactions and name the obtained products.
5. Which ions are found in a dilute solution of sodium tetraborate? Reason your answer.
6. Orthoboric acid solution does not react with sodium carbonate in the cold, while sodium tetraborate is produced with heating to boiling. Write down the equation for the corresponding reaction and explain why the reaction proceeds with heating and does not in the cold.
7. What substances are formed by the reaction between the following solutions: (a) $H_3BO_3 + NaOH$; (b) $Na_2B_4O_7 + NaOH$; (c) $Na_2B_4O_7 + H_2SO_4 + H_2O$; and during fusion of the following (a) $Cr_2O_3 + B_2O_3$; (b) $Na_4B_4O_7 + NiSO_4$. Write down the equations for the corresponding reactions.

8. What is the chemical composition of (a) borides; (b) boranes; and (c) borates? Write down the formula for each compound.
9. Overlapping of which electron orbitals accounts for the bond in the BCl_3 molecule? Draw the spatial configuration of the molecule.
10. Write down the equations for the reactions between aluminium and (a) dilute sulphuric and nitric acids; (b) concentrated sulphuric and nitric acids; (c) aqueous solution of sodium hydroxide.
11. Why does aluminium dissolve in an aqueous solution of sodium carbonate? Write down the equation for the corresponding reaction.
12. What solution should not be boiled in an aluminium container: sodium nitrate, mercury nitrate, sodium carbonate, or potassium chloride?
Reason your answer and write down the corresponding reaction equations.
13. Corundum is insoluble in acids, while the product of its fusion with alkali is readily soluble in acid. Write down the equations for the following: fusion of corundum with alkali and the reaction of the fusion product with sulphuric acid.
14. How can the amphoteric properties of aluminium hydroxide be experimentally demonstrated? Write down the equations for the corresponding reactions.
15. When excess potassium hydroxide and ammonium hydroxide react with aluminium sulphate, a substance precipitates which then dissolves only in one case. In which case? Write down the equations for the reactions.
16. By the action of what reagent can Al^{3+} ions be converted into $[Al(OH)_6]^{3-}$? Write down the ionic and molecular equations for the reaction.
17. How can aluminium sulphate be obtained from $Na_3[Al(OH)_6]$? Write down the ionic and molecular equations for the reactions.
18. What is the composition of aluminium ammonium sulphate? Write down the formula and the equation for its dissociation in a solution. What is the reaction of its aqueous solution? Explain.
19. A solution containing aluminium sulphate and sodium acetate is boiled. What substance precipitates? Write down the reaction equation.
20. Write down the equation for the hydrolysis of potassium aluminate.
21. What happens if excess hydrochloric acid is added gradually to a solution of potassium aluminate? What aluminium compounds are formed in this reaction? Write down the equations for the corresponding reactions.
22. What reaction occurs in an aqueous solution containing Al^{3+} and S^{2-} ions? Write down the corresponding reaction equations.
23. What is the difference between the reactions of chlorides of boron and aluminium with water? Write down the corresponding reaction equations.
24. Which oxidation states are demonstrated by gallium, indium and thallium? Which oxidation state is more stable for each of these elements?
25. Which of the following oxides is a stronger oxidant: Ga_2O_3, In_2O_3, or Tl_2O_3?
26. How do gallium, indium and thallium react with (a) concentrated hydrochloric acid, (b) concentrated nitric acid, (c) sodium hydroxide? Write down the equations for the corresponding reactions.
27. How does the strength of bases change in the following series: $Ga(OH)_3$, $In(OH)_3$, $Tl(OH)_3$? Write down the equations for the reactions demonstrating basic (?) or amphoteric (?) properties of said hydroxides.
28. How do the chlorides of gallium(III) and thallium(III) react with excess sodium hydroxide? Write down the equations for the corresponding reactions.
29. Write down the equation for the reaction by which the thiosalt of indium(III) is obtained from its chloride.

Examples of Multiple-choice Questions

1. The BF_3 molecule has a triangular form. What type of hybridization does it correspond to?
(1) sp^1; (2) sp^3; (3) sp^2; (4) p^3; (5) none.
2. What compound is produced by the reaction between boron and concentrated hitric acid?
(1) $B(NO_3)_3$; (2) B_2O_3; (3) $H_2B_4O_7$; (4) H_3BO_3; (5) HBO_2.
3. By the action of what substance can the ion $[Al(OH)_6]^{3-}$ be converted into $Al(OH)_3$?
(1) NaOH; (2) H_2SO_4; (3) $NH_3 \cdot H_2O$; (4) H_2O; (5) Na_2SO_4.
4. What aluminium compound is produced by the reaction between aqueous solutions of aluminium chloride and ammonium sulphide?
(1) Al_2S_3; (2) $Al_2(SO_4)_3$; (3) $Al(OH)_3$; (4) $Al(OH)_2Cl$; (5) $(NH_4)_3[Al(OH)_6]$.
5. Complete the reaction and select an appropriate coefficient for nitric acid in the reaction

$$Al + HNO_3 = NH_4NO_3 + \ldots$$

(1) 24; (2) 3; (3) 30; (4) 8; (5) 27.

EXPERIMENT 38. BORON

Apparatus and reagents

Water bath.
Ring stand. Glass rods. Platinum loop. Porcelain rod. Boric acid. Borax. Magnesium, ribbon or powder. Cobalt nitrate, crystals, powder. Chromium sulphate. Litmus, neutral solution. Universal indicator. Litmus paper, blue.
Methyl alcohol. Glycerol. Solutions: sulphuric acid, density 1.84 g/cm³; silver nitrate, 0.1 *N*; copper sulphate, 0.5 *N*; aluminium sulphate, 0.5 *N*; borax, 0.5 *N*, hot saturated solution, cold saturated solution. Hot saturated solution of borax (34 g of the salt per 100 ml of water) should be prepared by the laboratory assistant in a beaker and maintained hot (80°C) in a water bath for common use in the laboratory.

1. Preparing Boric Acid

Procedure. Place 5-6 drops of hot saturated solution of borax $Na_2B_4O_7 \times 10H_2O$ in a test tube and add 2-3 drops of concentrated sulphuric acid. Observe rapid precipitation of crystals of orthoboric acid.

Recording the results. Write drown the equation for the reaction by which boric acid is prepared from sodium tetraborate and sul-

phuric acid. Sodium tetraborate is the salt of what acid? Write down the formula of this acid.

2. Properties of Boric Acid

Procedure. Dissolve, with heating, a few crystals of boric acid in each of three test tubes, taking 5-8 drops of distilled water. Add 3-5 drops of neutral litmus solution into one test tube and observe the colour change. Drop a piece of magnesium ribbon or a microspatula of magnesium powder to the second test tube and observe liberation of gas. What is this gas?

Put a strip of universal indicator paper into the third test tube for a few seconds and compare its colour with the standard colour scale.

Draw your conclusion on the pH of the solution of boric acid.

Recording the results. Write down the equations for (a) the reaction between boric acid and magnesium; (b) dissociation of boric acid. Write down the pH of the obtained solution of boric acid and the dissociation constant for the first stage (see Table 7 of Appendix). Is boric acid a strong or weak electrolyte?

3. Specific Reactions for Boric Acid

A. Colouring flame

Procedure. Heat a porcelain rod in the flame of a burner and note the colour of the flame. Dip the hot rod in boric acid powder and put it again in the flame (at the edge of the outer cone). Observe the colour change of the flame.

B. Preparing trimethyl borate and its burning

Procedure. Place 3-4 crystals of $Na_2B_4O_7$ into a crucible and add 2-3 drops of concentrated sulphuric acid (density 1.84 g/cm^3) and 5-6 drops of methyl alcohol. Stir the mixture using a glass rod and light the evolving trimethyl borate $B(OCH_3)_3$. Note the colour of the flame.

Recording the results. Write down the equations for (a) the formation of boric acid, and (b) preparing trimethyl borate by the reaction between methyl alcohol and boric acid.

Concentrated sulphuric acid binds the formed water thus preventing hydrolysis of the ester.

Methyl alcohol can be replaced in this reaction by a trihydric alcohol, glycerol $C_3H_5(OH)_3$. Using a platinum loop, take a few crys-

tals of boric acid, wet with a drop of concentrated sulphuric acid and a drop of glycerol. Introduce the loop into the flame of the burner and observe intense green colouration of the flame.

4. Hydrolysis of Sodium Tetraborate

Procedure. Place 5-6 drops of neutral litmus solution into a test tube and add 3-4 drops of $Na_2B_4O_7$ solution. How does the colour of litmus change?

Recording the results. Write down the equations for stepped hydrolysis of sodium tetraborate taking into account that orthoboric acid and sodium metaborate are the products of the first hydrolysis step, and orthoboric acid and sodium hydroxide are produced in the second step of hydrolysis.

5. Preparing Sparingly Soluble Borates

Procedure. Place 3-4 drops of saturated solution of $Na_2B_4O_7$ into each of three test tubes and add a few drops of silver nitrate solution into the first test tube, of copper sulphate solution into the second, and of aluminium sulphate solution into the third test tube. Note the colour of the precipitates.

Recording the results. Write down the equations for the reactions, keeping in mind that water is involved and boric acid is produced in all reactions. The precipitates are silver metaborate, the basic salt of copper $CuOHBO_2$, and aluminium hydroxide, respectively. Explain why neutral salts, copper borate and aluminium borate, are not produced in the last two test tubes? Explain your answer and give the equations for the corresponding reactions.

6. Preparing Borax Pearls

Borates of certain metals are specifically coloured. Their solutions in molten borax form coloured glass (pearls) on cooling.

A. Preparing $Co(BO_2)_2$ pearl

Procedure. Place a few crystals of borax on a slide and, at a distance, a small quantity of powdered cobalt nitrate. Heat a platinum loop in the flame of a burner and touch the borax crystals with it. Heat the wire with the crystals again to fuse them into a clear vitreous mass. Cool this drop slightly and touch the powdered cobalt nitrate with it so that a small quantity of this salt sticks to it. Heat the wire again to prepare a homogeneous vitreous mass. Cool the pearl and note its colour.

Recording the results. Write down the equations for the decomposition of sodium tetraborate into sodium metaborate and boron oxide, and for the interaction between boron oxide and cobalt nitrate to form cobalt metaborate and nitrogen(V) oxide.

Write down the overall equation for the reaction between borax and cobalt nitrate.

Clean the platinum wire after the experiment is over. To do so, crush the pearl, wash the wire with hydrochloric acid, and calcine in the flame of the burner.

B. Preparing $Cr(BO_2)_3$ pearl

Procedure. Act as instructed in the previous test *A*, using chromium sulphate instead of cobalt nitrate.

Recording the results. Write down the equations for the decomposition of sodium tetraborate and for the reaction between boron oxide and chromium sulphate. Write down the overall equation for the reaction between borax and chromium sulphate.

Clean the wire as instructed above.

EXPERIMENT 39. ALUMINIUM. GALLIUM. INDIUM

Apparatus and reagents

Water bath.
Asbestos-centred gauze. Filter paper. Emery paper. Gallium (metal). Indium (metal).
Aluminium, powder, foil or wire. Iodine, crystals. Sulphur, powder. Potassium sulphate. Ammonium chloride.
Solutions: litmus, neutral; sodium hydroxide, 2 *N*; hydrochloric acid, 2 *N*, density 1.19 g/cm^3; sulphuric acid, 2 *N*, density 1.84 g/cm^3; nitric acid, 2 *N*, density 1.4 g/cm^3; aluminium chloride, 0.5 *N*; aluminium sulphate, 0.5 *N*; copper sulphate, 0.5 *N*; mercury(I) nitrate, 0.5 *N*, copper chloride, 0.5 *N*; ammonium (or sodium) sulphide, 0.5 *N*; gallium chloride, 0.5 *N*; indium chloride, 0.5 *N*.

1. Reaction of Aluminium with Acids

A. Reaction of aluminium with dilute acids

Procedure. Place 5-8 drops of 2 *N* solutions of acids: hydrochloric into the first test tube, sulphuric into the second, and nitric acid into the third test tube. Drop a small piece of aluminium foil into each acid. Does the reaction take place in all three test tubes in the

cold? Now heat the test tubes in a water bath and observe the reaction. Write down the equations for the corresponding reactions. What gas is liberated when aluminium reacts with dilute nitric, sulphuric or hydrochloric acid?

B. Reaction of aluminium with concentrated acids

Procedure. Act as instructed in the previous test *A*, except that use concentrated hydrochloric, sulphuric and nitric acids instead of the dilute acids. The densities of the acids should be 1.19, 1.84, and 1.4 g/cm^3, respectively. Does the reaction take place in the cold? Which acid does not act on aluminium? Why? Heat the test tubes in a water bath and observe the reaction.

Recording the results. Describe your observations and answer the questions. Write down the reaction equations, taking into account that nitric acid is reduced mainly to nitrogen dioxide with heating, while sulphuric acid is reduced to sulphur dioxide in the cold and partly to free sulphur with heating. Does the concentration of hydrochloric acid influence the reaction with aluminium?

C. Passivation of aluminium

Procedure. Place 5-6 drops of hydrochloric acid into a test tube and add a piece of aluminium foil. Observe evolution of hydrogen. Remove aluminium from the test tube, rinse with water, and put into concentrated nitric acid (density 1.4 g/cm^3) for 2-3 minutes. Remove the aluminium from the acid, rinse with water, and put it again into the hydrochloric acid. Does hydrogen evolve? Does aluminium dissolve? What has happened to aluminium?

2. Dissolution of Aluminium in Alkali Solution

Procedure. Place a strip of aluminium foil into a test tube and add 3-4 drops of water. Heat the test tube in a water bath. Does hydrogen evolve? Add 5-8 drops of 2 *N* sodium hydroxide solution. Observe intense liberation of hydrogen.

Recording the results. Aluminium does not react with water because a dense oxide film is formed on the aluminium surface which prevents hydrogen ions from contact with the metal. When an alkali is added, the oxide film is dissolved in it and a corresponding hydroxy aluminate is formed. Aluminium can now react with water. The reaction proceeds according to this scheme:

(1) $Al_2O_3 + NaOH + H_2O \rightarrow Na_3[Al(OH)_6]$
(2) $Al + H_2O \rightarrow Al(OH)_3 + H_2$
(3) $Al(OH)_3 + NaOH \rightarrow Na_3[Al(OH)_6]$

Place proper coefficients into these equations.

3. Interaction of Amalgamated Aluminium with Water

As aluminium reacts with a mercury salt, amalgam is formed on the metal surface. The dense structure of the protective film on aluminium surface is thus destroyed and the metal becomes chemically active. It reacts vigorously with water to liberate hydrogen.

Procedure. Clean a strip of aluminium with abrasive paper, rinse with water, dry with filter paper, and place into a test tube half filled with distilled water. Does hydrogen liberate? Rub carefully the aluminium with a glass rod: does any gas evolve now?

Remove the aluminium from the test tube, wipe it dry, place on a piece of filter paper and wet with a drop of mercury(I) nitrate solution $Hg_2(NO_3)_2$. After 2-3 minutes, dry the aluminium with filter paper and dip again in distilled water in the test tube. Observe the reaction. Rub the aluminium surface with a glass rod and observe liberation of hydrogen. Write down the equation for the reaction between aluminium and mercury(I) nitrate and also between aluminium and water.

4. Effect of the Chloride Ion on Aluminium Corrosion

The chloride ion is a strong activator of corrosion. It promotes destruction of the protective film of aluminium oxide in a solution, thus intensifying corrosion.

Procedure. Place a piece of aluminium into each of two test tubes and add 5-8 drops of copper sulphate solution into one and the same amount of copper chloride into the other test tube. Observe the different reaction: aluminium remains almost unchanged in the first test tube and rapidly becomes coated with copper in the other test tube.

Write down the equations for the corresponding reactions.

5. Reaction of Aluminium with Nonmetals

A. Reaction of aluminium with iodine
(Use the hood when carrying out tests 5A and 5B.)

Procedure. Place a microspatula of fine powder of iodine and of aluminium powder into a crucible or a porcelain dish. Stir the mixture thoroughly using a glass rod. Add 1-2 drops of distilled water. Observe evolution of the iodine vapour.

Recording the results. Write down the reaction equation. Note the heat effect of the reaction. (Water acts as a catalyst in this reaction.)

B. Reaction of aluminium with sulphur

Procedure. Place 5-6 microspatulas of aluminium powder and the double quantity of powdered sulphur (sulphur flowers) on a sheet of filter paper and mix thoroughly. Transfer the mixture onto an asbestos-centred gauze in the stand ring over a burner. Heat the mixture stirring it with a glass rod. Flashes can be observed because the reaction between aluminium and sulphur is exothermic. When the reaction is over (no more flashes), put the burner aside. Cool the aluminium sulphide and transfer it into a test tube. Save it for test 7*B*.

Write down the equation for the reaction by which aluminium sulphide is prepared.

6. Preparing Aluminium Hydroxide and Studying Its Properties

Procedure. Place 2-3 drops of an aluminium salt solution into each of two test tubes and add 2-3 drops of 2 *N* sodium hydroxide solution to both: observe precipitation of aluminium hydroxide. Add 3-5 drops of a 2 *N* solution of hydrochloric acid to the precipitate in one test tube and the same amount of a 2 *N* solution of sodium hydroxide to the other test tube. Observe the reaction in the test tubes.

Recording the results. Characterize the properties of aluminium hydroxide.

Write down the equations for the reaction by which aluminium hydroxide is prepared and the reaction of aluminium hydroxide with hydrochloric acid and sodium hydroxide. The complex anion $[Al(OH)_6]^{3-}$ is formed in the alkaline medium. Name the obtained aluminium compounds. Write down the equation for dissociation of aluminium hydroxide. How does the concentration of Al^{3+} and $[Al(OH)_6]^{3-}$ ions change when acid or alkali is added?

7. Hydrolysis of Aluminium Salts

A. Hydrolysis of aluminium chloride

Procedure. Place 5-6 drops of a neutral litmus solution into a test tube and add 1-3 drops of aluminium chloride. Observe the change of litmus colour and explain this.

Recording the results. Write down the ionic and molecular equations for the hydrolysis occurring mostly at the first step. Why does the hydrolysis of this salt not proceed to the end? How can the degree of hydrolysis of this salt be decreased?

B. Hydrolysis of aluminium sulphide

Procedure. Add 5-8 drops of water to the test tube containing aluminium sulphide prepared in test 5*B*: observe evolution of gas. Identify the gas by its odour. Which aluminium compound is formed?

Recording the results. Write down the ionic and molecular equations for the reaction between aluminium sulphide and water. Explain why the hydrolysis is practically irreversible in this case.

C. Joint hydrolysis of aluminium chloride and ammonium sulphide

Procedure. Place 2-3 drops of an aluminium salt solution into a test tube and add the same amount of ammonium sulphide solution. Observe precipitation of aluminium hydroxide and liberation of hydrogen sulphide.

Recording the results. Write down the equation for the joint hydrolysis of the two salts. Why does the hydrolysis proceed to the end in this case? Will a similar reaction occur in an aqueous solution, if sodium sulphide is used instead of ammonium sulphide? Can aluminium carbonate be obtained by an exchange reaction between two corresponding salts in an aqueous solution?

8. Reaction of Gallium and Indium with Acids

Procedure. Place a small piece of gallium metal into each of three test tubes and add 3-5 drops of concentrated hydrochloric acid (density 1.19 g/cm^3) to one test tube, sulphuric acid (density 1.84 g/cm^3) to another, and nitric acid (density 1.4 g/cm^3) to the third test tube. Does the reaction occur in the cold? Heat the test tubes in a water bath. What gas liberates during dissolution of gallium in hydrochloric acid? What gases are evolved in the reaction of gallium with sulphuric and nitric acids?

Conduct a similar experiment with indium. Do gallium and indium react with acids in the same way? Write down the equations for the reactions. Gallium and indium are oxidized to their tervalent state in all reactions.

9. Reaction of Gallium and Indium with Alkali

Procedure. Place 5-6 drops of 6 *N* sodium hydroxide solution into each of two test tubes and add a small grain of gallium into one, and the same amount of indium into the other test tube. Heat carefully over a low flame of the burner or in a water bath. Observe the reaction in the test tubes.

Recording the results. Note the different properties of gallium and indium. Which metal is more like aluminium with respect to its

properties? Write down the equation for the reaction between gallium and sodium hydroxide with liberation of hydrogen and formation of sodium tetrahydroxygallate $Na_3[Ga(OH)_6]$. Can a similar reaction occur with indium?

10. Gallium and Indium Hydroxides

Procedure. Place 5-6 drops of gallium salts into each of two test tubes and add carefully, drop by drop, sodium hydroxide solution to precipitate gallium hydroxide. Prove its amphoteric properties experimentally. Observe the reaction in each case. Repeat the experiment using an indium salt. What is the reaction of indium hydroxide to acid? What properties are demonstrated by indium hydroxide?

Recording the results. Describe your observations. Compare the properties of the hydroxides of gallium and indium. Write down the equations for (a) the reactions of formation of the hydroxides $Ga(OH)_3$ and $In(OH)_3$; (b) the reaction of the obtained hydroxides with acid and alkali (the complex anion $[Ga(OH)_6]^{3-}$ and the corresponding salt are produced in an alkaline medium). Name the obtained compounds.

EXPERIMENT 40. SYNTHESIS OF ALUMINIUM POTASSIUM SULPHATE

Apparatus and reagents

Chemical balance. Set of weights. Watch glasses. Beakers, 100-ml. Glass rods. Büchner funnel. Bunsen flask. Water-jet pump. Ring stand. Filter paper. Spatula. Asbestos-centred gauze. Microscope. Glass slide. Potassium sulphate. Aluminium sulphate, crystalline. Distilled water.

Procedure. Weigh out 1.74 g of potassium sulphate and 6.66 g of aluminium sulphate. Place 7 ml of distilled water into one beaker and 6 ml into another. Cover the beakers with watch glasses and heat to boiling. Dissolve the weighed potassium sulphate in the first and aluminium sulphate in the second beaker. Pour the hot solutions together (into the beaker containing potassium sulphate) and mix them. A double salt of potassium aluminium sulphate is thus produced:

$$K_2SO_4 + Al_2(SO_4)_3 \cdot 18H_2O + 6H_2O = 2KAl(SO_4)_2 \cdot 12H_2O$$

Cool rapidly with continually stirring the mixture: fine crystals of the alum precipitate. If large crystals are wanted, allow the solution to cool slowly without stirring. Transfer the crystals onto a Büchner funnel, separate them from the liquid, and dry between filter papers. Leave them to dry in air and weigh to determine the yield of the alum in per cent.

Transfer a few fine crystals onto a glass slide and examine under a microscope. Draw sketches of the crystals in your log-book. Test the double salt for the presence of Al^{3+} and SO_4^{2-} ions using the known reactions. Write down the equation for dissociation of the obtained substance. Describe your experiment.

17 Elements of Subgroup IIB

QUESTIONS AND PROBLEMS

1. Write down the electron formulas for the atoms of zinc and cadmium. In which of these elements are the metal properties more pronounced? Explain.

2. Write down the equations for the reactions of zinc dissolution in (a) hydrochloric acid; (b) sulphuric acid (concentrated and dilute); (c) nitric acid (concentrated and dilute); (d) alkali.

3. Which of the hydroxides, $Zn(OH)_2$ or $Cd(OH)_2$, has a stronger basic properties? Reason your answer.

4. Write down an equilibrium diagram for the system precipitate-solution of zinc hydroxide and indicate the direction in which this equilibrium will be shifted when acid or alkali is added.

5. What ions are produced during dissociation of $Zn(OH)_2 \cdot 2KOH$ in an aqueous solution?

6. Write down the formulas of various salts formed by zinc hydroxide.

7. By what reactions can the following ions be differentiated in a solution: (a) Zn^{2+} and Cd^{2+}; (b) Hg^{2+} and Hg_2^{2+}? Write down the equations for the corresponding reactions.

8. Write down the equations for the reactions occurring in solutions containing the Zn^{2+}, Cd^{2+}, and Hg^{2+} ions, if (a) excess alkali, (b) excess ammonia solution are added to them.

9. Write down the coordination formulas for the following compounds (a) $Zn(OH)_2 \cdot 2KOH$; (b) $Cd(OH)_2 \cdot 4NH_3$; (c) $2KI \cdot HgI_2$. Name these compounds.

10. Which of the salts, $ZnCl_2$ or $[Zn(NH_3)_4]Cl_2$ (1 *N* solution) has a higher degree of hydrolysis? Explain your answer.

11. Which solution, H_2S or $(NH_4)_2S$, will ensure a more complete precipitation of zinc sulphide from a solution? Explain your answer.

12. What type of complexes, internal- or external orbital are the following compounds: (a) $[Zn(NH_3)_4]Cl_2$; (b) $[Cd(NH_3)_4]Cl_2$? Are they dia- or paramagnetic? What is the configuration of their molecules?

13. What happens if a solution of mercury(II) nitrate is treated with excess potassium iodide? Write down the reaction equation.

14. Write down the equation for dissolution of mercury in concentrated nitric acid (in excess and in a small amount of the acid).

15. Give examples of reactions in which (a) zinc is a reductant; (b) Hg^{2+} is an oxidant; (c) Hg_2^{2+} is a reductant.

16. Consult the table of oxidation-reduction potentials and decide in which medium zinc is a stronger reductant.

17. Calculate the standard enthalpy of reduction of zinc oxide with carbon monoxide (consult the tables of Appendix).

Examples of Multiple-choice Questions

1. What is the pH of a zinc nitrate solution?
(1) <7; (2) about 7; (3) about 10; (4) about 12; (5) about 14.
2. Determine the sum of coefficients in the left part of the equation for the reaction between zinc and alkali solution.
(1) 2; (2) 12; (3) 3; (4) 5; (5) 8.
3. What is the configuration of the hydroxy complex of zinc?
(1) square; (2) pyramid; (3) octahedron; (4) tetrahedron; (5) triangle.
4. What substance precipitates when excess of concentrated KI acts on $Hg_2(NO_3)_2$ solution?
(1) Hg_2I_2; (2) Hg, I_2; (3) HgI_2, Hg; (4) Hg.
5. What substances precipitate if excess of concentrated KOH acts on the solution containing $Zn(NO_3)_2$, $Cd(NO_3)_2$, $Hg_2(NO_3)_2$?
(1) $Zn(OH)_2$, $Cd(OH)_2$, Hg; (2) $Cd(OH)_2$, HgO, Hg; (3) $Cd(OH)_2$, Hg_2O; (4) $Cd(OH)_2$, $Hg_2(OH)_2$; (5) $Cd(OH)_2$, HgO.

EXPERIMENT 41. ZINC. CADMIUM

Apparatus and reagents

Porcelain crucible.
Asbestos-centred gauze.
Zinc sulphate. Cadmium sulphate.
Zinc, powder and granules.
Sulphur (flowers). Litmus paper, red. Litmus, neutral solution.
Solutions: sulphuric acid, 2 *N*; density 1.84 g/cm³; hydrochloric acid, 2 *N* and 1 *N*; sodium hydroxide, 2 *N*; potassium hydroxide, concentrated; ammonia solution, 2 *N*; cadmium sulphate, 2 *N*; zinc sulphate, 2 *N*; potassium nitrate, 0.5 *N*; sodium carbonate, 0.4 *N*; ammonium sulphide, saturated.

1. Dissolution of Zinc in Acids and Alkalies

Procedure. Place 4-5 drops of 2 *N* sulphuric acid solution into a test tube and add a microspatula of zinc dust. Heat the test tube slightly. Repeat the experiment using concentrated sulphuric acid (density 1.84 g/cm³). Identify sulphur dioxide gas by its odour.

Act similarly to investigate solubility of zinc in 2 *N* hydrochloric acid and in 2 *N* alkali solution.

Recording the results. Describe your observations. Why does zinc differently react with dilute and concentrated sulphuric acid? Which atom and in which oxidation state acts as an oxidizer in either of these cases?

2. Reducing Properties of Zinc

Procedure. Place a small amount of zinc dust into a porcelain crucible, add 4 drops of a 0.5 *N* solution of potassium nitrate and 4-5 drops of concentrated alkali solution. Heat carefully on an asbestos-centred gauze almost to boiling. Note liberation of ammonia (by odour and by bluing of red moist litmus paper). Which salt of zinc is produced under these conditions?

Recording the results. Answer the questions. Write down the ionic and molecular equations for the reaction. Pay attention to the high reducing power of zinc. Write down the corresponding oxidation-reduction potentials and decide if zinc will reduce potassium dichromate in an acidic medium.

3. Hydroxides of Zinc and Cadmium

Procedure. Place 3-4 drops of a zinc salt solution into each of two test tubes and the same amount of a cadmium salt solution into two other test tubes. Add, drop by drop, 2 *N* alkali solution to each of four test tubes to precipitate jelly-like hydroxides of zinc and cadmium. Try the action of acids and alkalies on the obtained hydroxides.

Recording the results. Characterize the properties of the hydroxides of zinc and cadmium. Write down the ionic and molecular equations for the corresponding reactions. Explain the different properties of the hydroxides.

4. Sulphides of Zinc and Cadmium

Procedure. Place 3-4 drops of a zinc salt solution into one test tube and the same amount of a cadmium salt solution into the other test tube. Add 2-3 drops of a saturated ammonium sulphide solution to each test tube. Note the colour of the precipitates. Add a drop of 1 *N* hydrochloric acid to each test tube. Which of the sulphides is more readily soluble in the acid?

Recording the results. Use the solubility product rule to explain the different solubility of the sulphides of zinc and cadmium in acid. Write down the reaction equations.

5. Hydrolysis of Zinc and Cadmium Salts

Procedure. Place a few crystals of a zinc salt into one test tube and the same amount of a cadmium salt into another test tube. Dissolve the salts in 1-2 drops of water and add 2-3 drops of a litmus solution to both. Heat slightly the solutions. Place 2-3 drops of a litmus solution into the third test tube and add 1-2 drops of water. Compare the colour of this solution with those of the two solutions prepared earlier. Is the medium of the salt solutions acidic or alkaline? Write down the ionic and molecular equations for the reactions responsible for the colour change of litmus.

6. Complex Compounds of Zinc and Cadmium

Procedure. Place a drop of a zinc salt solution into a test tube and add two drops of 2 *N* ammonia solution. What substance precipitates? Add, drop after drop, excess ammonia solution to dissolve the precipitate. Repeat the experiment using a cadmium salt instead of the zinc salt.

Recording the results. Write down the equations for the reactions, assuming that the characteristic coordination number for both complexing ions is 4. Write down the equations for dissociation of the obtained complex compounds and complex ions, and also their instability constants. Consult Table 12 of Appendix, write down the instability constants of the complexes, and explain the different stability of the obtained complex ions.

EXPERIMENT 42. SYNTHESIS OF CADMIUM CARBONATE AND DETERMINING CO_2 CONCENTRATION IN IT

Apparatus and reagents

Two beakers, 100-ml. Crystallizer. Büchner funnel. Test tube with a gas-discharge tube. Graduated cylinder, 50-ml. Apparatus for determining equivalent weight of a metal.
Cadmium sulphate. Sodium carbonate.

Procedure. Weigh out 14 g of cadmium sulphate on a chemical balance, transfer the salt into a beaker (100-ml) and add water by small portions. Dissolve the salt by stirring the solution using a glass rod.

Calculate the stoichiometric quantity of sodium carbonate which is necessary to prepare cadmium carbonate. Weigh the wanted quantity and dissolve it in another 100-ml beaker. Heat the second solution to boiling slowly and add the first solution (cadmium sulphate) to it. Place the beaker in a crystallizer filled with cold water, cool

the solution, and filter the precipitated cadmium carbonate on a Büchner funnel. Dry the precipitate between the filter paper and then in a drying cabinet at a temperature not above 100° C (the salt decomposes at higher temperatures). Weigh the dry salt and determine the yield.

The content of CO_2 in the salt can be determined by the volume of carbon dioxide evolving during decomposition of $CdCO_3$. (For the determination of CO_2 volume, see Experiment 6).

EXPERIMENT 43. MERCURY

Mercury and all its compounds are poisons!
After the experiment is over, all test tubes that were used for the experiment with mercury or its compounds should be handled over to the laboratory assistant. Wash the hands thoroughly.

Apparatus and reagents

Microscope.
Porcelain crucible. Mercury(II) oxide.
Solutions: nitric acid, density 1.4 g/cm³; sodium hydroxide, 2 *N*; ammonium sulphide, saturated; mercury(II) nitrate, 2 *N*; mercury(I) nitrate, 2 *N*; sodium chloride, saturated, 0.5 *N*; potassium iodide, 0.5 *N* and 0.2 *N*; potassium thiocyanate, saturated; silver nitrate, 2 *N*; cobalt chloride, saturated; tin(II) chloride, 0.5 *N*; ammonia solution, 2 *N*; hydrogen sulphide solution.

1. Reaction of Mercury Salts with Alkali

Procedure. Place 3 drops of mercury(II) nitrate solution into a test tube and the same amount of mercury(I) nitrate solution into the other test tube. Add two drops of 2 *N* alkali solution to both and observe precipitation of mercury(II) oxide HgO in the first test tube. The precipitate in the second test tube is a mixture of products of disproportionation of mercury(I) oxide: mercury(II) oxide and metal mercury. Note the colour of the precipitates and write down the equations for the reactions.

2. Sparingly Soluble Mercury Salts

A. Preparing mercury chlorides

Procedure. Prepare mercury(II) chloride in one test tube and mercury(I) chloride in the second test tube by the reaction between 0.5 *N* sodium chloride and the corresponding mercury nitrate.

Recording the results. Compare solubility of the sublimate $HgCl_2$ and calomel Hg_2Cl_2. Write down the reaction equations.

B. Preparing mercury iodides

Procedure. Prepare mercury(II) and mercury(I) iodides by acting with 0.5 *N* potassium iodide solution on the corresponding mercury nitrates contained in two separate test tubes. (Potassium iodide solution should be added drop after drop, until the iodides precipitate.)

Note the colour of the precipitates.

Recording the results. Write down the equations for the reactions taking into consideration that Hg_2^{2+} ion tends to undergo disproportionation with formation of Hg^{2+} and free mercury.

C. Action of hydrogen sulphide on mercury salts

Procedure. Act with hydrogen sulphide water on solutions of mercury(II) and mercury(I) nitrates contained in two separate test tubes. Note the colour of the precipitates.

Write down the equations for the reactions observed, taking into account the fact that mercury(I) sulphide is quite unstable and when hydrogen sulphide solution is added, mercury(II) sulphide and metal mercury are formed.

3. Complex Mercury Compounds

A. Reaction of mercury(II) nitrate with excess potassium iodide

Procedure. Place 1-2 drops of mercury(II) nitrate into a test tube and precipitate mercury iodide by adding 2 drops of potassium iodide solution. Add excess potassium iodide (10-12 drops). What happens to the precipitate? Characterize the solubility of the obtained complex compound $HgI_2 \cdot 2KI$. Write down the coordination formula of this compound bearing in mind that Hg^{2+} ion has the coordination number of 4. Add 2 drops of silver nitrate solution to the obtained solution. What is the solubility of the obtained complex compound $Ag_2[HgI_4]$?

Recording the results. Answer the questions and name the complex salts. Write down the ionic and molecular equations for the reactions. Write down the instability constant for the obtained complex anion.

B. Reaction of mercury(II) nitrate with excess potassium thiocyanate

Procedure. Place 2-3 drops of mercury(II) nitrate in a test tube and add 4-5 drops of a saturated potassium thiocyanate solution. Write down the coordination formula of the obtained complex compound $Hg(SCN)_2 \cdot 2KSCN$. Add 2-3 drops of a saturated cobalt chloride solution. The following reaction occurs:

$$K_2[Hg(SCN)_4] + CoCl_2 = Co[Hg(SCN)_4] + 2KCl$$

Recording the results. Write down the ionic equation for the reaction. Note the colour of the formed precipitate. Name the complex compounds obtained during the experiment.

C. Reaction of mercury salts with ammonium hydroxide

Procedure. Place 2 drops of mercury(II) nitrate solution into a test tube and the same amount of mercury(I) nitrate into the second test tube. Add 1-2 drops of 2 *N* ammonium hydroxide solution to both: observe precipitation of white ammonium mercury nitrate $[Hg_2ONH_2]NO_3$ in the first test tube, a black precipitate of metal mercury can be seen in the second test tube; the mercury is formed along with ammonium mercury nitrate according to the following equation:

$$2Hg_2(NO_3)_2 + 4NH_3 + H_2O = [Hg_2ONH_2]NO_3 + 2Hg + 4NH_4NO_3$$

The decomposition $Hg_2^{2+} \rightarrow Hg^{2+} + Hg$ is so much accelerated in the presence of ammonia, that it is practically impossible to prepare an ammonia derivative of mercury(I).

How do the reactions of ammonia with mercury salts differ from those with zinc and cadmium salts?

4. Oxidizing Properties of Mercury Salts

Procedure. Place 2 drops of mercury(II) nitrate solution into a test tube and add 3 drops of 0.5 *N* tin chloride solution. After addition of the first drop, observe precipitation of white calomel Hg_2Cl_2. The precipitate darkens in 3-4 minutes. Why? Write down the equations for the reactions observed.

5. Reducing Properties of Mercury(I) Salts

Procedure. Place 7-8 drops of mercury(I) nitrate solution into a porcelain crucible and add 2 drops of concentrated nitric acid (density 1.4 g/cm^3). Boil for 1-2 minutes, then cool the liquid and transfer it using a pipette into a test tube. Place an equal volume of mercury(I) nitrate into another test tube and add 2 drops of a saturated sodium chloride solution to both test tubes. How do the solutions differ in their behaviour? How can this difference be explained? Write down the equations for the reactions. Answer the questions.

18 Elements of Subgroup IB

QUESTIONS AND PROBLEMS

1. Indicate the position of copper and silver in the periodic table and draw the electron formulas of their atoms. Why are copper and silver weaker reductants than the alkali metals?
2. What happens if (a) dilute hydrochloric acid; (b) dilute nitric acid; or (c) concentrated nitric acid act on copper? Write down the equations for the corresponding reactions.
3. Describe the reaction of copper with (a) dilute sulphuric acid; (b) concentrated sulphuric acid with heating?
4. Write down the reaction in which basic copper carbonate $(CuOH)_2CO_3$ is produced when water vapour, oxygen and carbon dioxide act on copper.
5. Copper(II) hydroxide is soluble in dilute acids and in ammonia solution. Are these reactions similar? Write down the ionic and molecular equations for the corresponding reactions.
6. Which base, $Cu(OH)_2$ or $[Cu(NH_3)_4](OH_2)$, has a stronger basic character? Explain your answer.
7. Does silver(I) oxide have strongly basic or weakly basic properties if the reaction of a dilute silver nitrate solution is neutral?
8. Indicate the oxidant and the reductant in the reaction between silver oxide and hydrogen peroxide, if oxygen is evolved during the reaction. Write down the equation for the reaction.
9. Silver chloride is sparingly soluble in water and acids but it readily dissolves in ammonia solution. Why? Write down the ionic equation for the reaction and explain the dissolution process using the rule of solubility product.
10. Write down the formulas of cyano and ammino complexes of silver if the coordination number of silver is 2. How do the complex ions of silver in these two compounds differ?
11. Consult the Table of standard electrode potentials and decide if Fe^{2+} can reduce the following ions to free metals: (a) Cu^{2+}; (b) Ag^{+}; (c) $[Ag(NH_3)_2]^{+}$.

Examples of Multiple-choice Questions

1. Which acid can dissolve metal copper?
(1) HCl, dilute; (2) HCl, concentrated; (3) H_2SO_4, concentrated; (4) HNO_3, dilute; (5) HNO_3, concentrated.
2. Which copper salts are sparingly soluble in water?
(1) $CuCl_2$; (2) CuS; (3) $CuSO_4$; (4) $Cu(NO_3)_2$; (5) $(CuOH)_2CO_3$.
3. Which of the following formulas describes the complex cupric tetramminohydroxide?
(1) $[Cu(NH_3)](OH)_2$; (2) $[Cu(NH_3)_2]OH$; (3) $[Cu(NH_3)_3](OH)_2$; (4) $[Cu(NH_3)_4] \times (OH)_2$; (5) $Cu(NH_3)_4]OH$.
4. Which properties are exhibited by Ag_2O, if the solution of $AgNO_3$ reacts neutral?
(1) strongly basic; (2) weakly basic; (3) amphoteric; (4) non-salt-forming.
5. Put proper coefficients for the equation of the reaction below and indicate what theoretical volume, at STP, NO will occupy during dissolution of 10.8 g of silver in nitric acid:

$$Ag + HNO_3 \rightarrow AgNO_3 + NO + H_2O$$

(1) 22.4 l; (2) 11.2 l; (3) 0.75 l; (4) 7.47 l; (5) 5.6 l.

EXPERIMENT 44. COPPER

Apparatus and reagents

Microflask.
Apparatus for reduction of copper.
Copper(II) oxide. Charcoal powder.
Zinc granules. Copper wire and shavings.
Solutions: hydrogen sulphide solution, freshly prepared; starch; formaldehyde, 10%; nitric acid, 2 *N* density, 1.4 g/cm^3; sulphuric acid, 4 *N*, 2 *N*, density 1.84 g/cm^3; hydrochloric acid, 2 *N*, density 1.19 g/cm^3; sodium hydroxide or potassium hydroxide, 2 *N*; ammonia solution, 2 *N*; copper(II) sulphate, 0.5 *N*, copper(II) chloride, 0.5 *N*; sodium carbonate, 2 *N*; potassium iodide, 0.5 *N*; sodium thiosulphate, 0.5 *N*; sodium sulphite, 0.5 *N*.

1. Reduction of Copper(II) Oxide

A. Reduction of copper(II) oxide with carbon

Procedure. Place 2-3 microspatulas of copper(II) oxide on a sheet of clean paper and mix with an equal volume of charcoal powder. Transfer the mixture into a cylindrical test tube, fix it in the stand in the horizontal position, and heat over a strong flame for 5-10 minutes. Observe reduction of copper(II) oxide to metal copper (change of colour). Note that the mixture becomes hot red.

If a dense coat of copper is deposited on the test tube walls, add 2-3 drops of concentrated nitric acid and dissolve copper completely.

Write down the equation for the reduction of copper(II) oxide.

B. Reduction of copper(II) oxide with hydrogen

Procedure. Fix a microflask in the stand, fill it to 2/3 its capacity with a 4 *N* solution of sulphuric acid, and add a grain of zinc. Close the test tube with a stopper provided with a gas-discharge tube (see Fig. 25). A microspatula of copper(II) oxide powder should be placed in the tube knee beforehand. Pass hydrogen over the copper oxide for 1-2 minutes without heating. When all air is displaced from the apparatus by hydrogen, heat the copper(II) oxide in the tube with a low flame of the burner. Observe the reaction.

Write down the equation for the reduction of copper(II) oxide with hydrogen.

2. Reaction of Copper with Dilute and Concentrated Acids

Procedure. Place three grains of copper in each of three test tubes and add 5-6 drops of 2 *N* hydrochloric acid to the first test tube, of sulphuric acid to the second, and of nitric acid to the third test tube.

Have the solutions in the test tubes turned blue green, which is specific for Cu^{2+} ion?

Carry out a similar experiment with concentrated acids (hydrochloric acid, density 1.19 g/cm^3, sulphuric acid, density 1.84 g/cm^3, nitric acid, density 1.4 g/cm^3) with and without heating. (Be cautious when heating the solutions.) With which acid does copper react?

Recording the results. Write down the equations for the reactions of copper with dilute nitric acid assuming that nitric acid is reduced to NO. Why does copper not react with hydrochloric acid or dilute sulphuric acid?

Write down the equations for the reactions of copper with concentrated acids assuming that concentrated nitric acid is reduced with copper to nitrogen dioxide and sulphuric acid to sulphur dioxide.

3. Reaction of Copper(II) Oxide with Acids

Procedure. Place 2-3 microspatulas of copper(II) oxide into each of two test tubes and add 5-6 drops of 2 *N* hydrochloric acid into one test tube and of sulphuric acid into the other. Observe the colour change in both solutions.

Write down the equations for the reactions of copper(II) oxide with HCl and H_2SO_4.

4. Copper(II) Hydroxide

A. Preparing copper(II) hydroxide and its thermal decomposition

Procedure. Place 3-4 drops of copper(II) sulphate solution into a test tube and add the same amount of 2 *N* alkali solution. Note the colour of the precipitated cupric hydroxide. Heat the test tube carefully: how does the colour of the precipitate change as the hydroxide of copper(II) changes to the oxide? Save the solution for test 7 of this Experiment.

Write down the equations for the reactions by which cupric hydroxide is formed and decomposed.

B. Reaction of Copper(II) Hydroxide with Acids and Alkalies

Procedure. Prepare copper(II) hydroxide in each of two test tubes. Add 5-6 drops of 2 *N* sulphuric acid to one precipitate and the same amount of 2 *N* alkali solution to the other.

Recording the results. In which test tube does the precipitate dissolve? What is your conclusion about the properties of copper(II) hydroxide?

Note: Copper(II) hydroxide dissolves in excess concentrated alkali solution to give cuprates of the $Na_2[Cu(OH)_4]$ type. But these cuprates are unstable and when the solution is diluted they decompose with liberation of $Cu(OH)_2$. This indicates that the acidic properties of copper(II) hydroxide are very weak.

5. Sparingly Soluble Copper(II) Salts

A. Preparing copper(II) sulphide

Procedure. Place 2-3 drops of copper(II) sulphate or chloride solution into a test tube and add the same amount of hydrogen sulphide solution.

Recording the results. Note the colour of the precipitated copper(II) sulphide. Write down the ionic and molecular equations for the reaction by which it is formed.

B. Preparing basic copper(II) carbonate

Procedure. Place 2-3 drops of copper(II) sulphate solution into a test tube and add an equal volume of soda solution. Observe precipitation of green copper hydroxycarbonate $(CuOH)_2CO_3$. Explain why neutral copper carbonate does not precipitate when copper salts react with soda solution.

Write down the equation for the reaction between copper(II) sulphate and soda.

6. Preparing Copper(I) Iodide

Procedure. Place 3 drops of copper(II) sulphate into a test tube and add the same volume of potassium iodide. Observe precipitation and note the yellow colour of the test tube contents. Add starch solution to prove that the yellow colour is due to free iodine.

In order to identify the colour of the precipitated copper(I) iodide, it is necessary to convert free iodine, which masks the colour of the precipitate, into colourless ion. To do so, add a few drops of sodium sulphite solution until the yellow colour vanishes. Save the solution for test 8*A*.

Recording the results. What is the colour of copper(I) iodide? Write down the equations for the reactions: (a) between copper(II) sulphate and potassium iodide; (b) between iodine and sodium sulphite (in the presence of water).

Explain the stability of copper(I) iodide.

7. Preparing Copper(I) Oxide

Procedure. Place 3-4 drops of copper(II) chloride solution into a microflask and add 5-6 drops of a 10% formaldehyde solution HCHO. Heat the mixture to boiling. Add 4-5 drops of 2 *N* sodium hydroxide solution and observe precipitation of yellow (finely dispersed) copper(I) hydroxide. Observe the colour change. Continue boiling until the precipitate turns red, the colour characteristic of copper(I) oxide. Compare the colour of the obtained copper(I) oxide with that of copper(II) oxide prepared in test 4*A*.

Recording the results. Write down the equations for the following: (a) preparation of copper(I) hydroxide by reduction of copper(II) chloride with formaldehyde in an alkaline medium (formaldehyde HCHO is oxidized to formic acid HCOOH in this reaction; formic acid reacts with sodium hydroxide to give sodium formate HCOONa); (b) reaction by which copper(I) oxide is prepared from its hydroxide.

8. Complex Compounds of Copper

A. Preparing complex copper(I) thiosulphate

Procedure. Add a few drops of sodium thiosulphate solution to the test tube containing copper(I) iodide precipitate prepared in test 6. Observe complete dissolution of the precipitate due to formation of a readily soluble complex of copper(I) thiosulphate.

Recording the results. Write down the equation for the reaction, taking into account that $S_2O_3^{2-}$ ions are monodentate ligands, and that the coordination number of Cu^+ ion is 2.

B. Preparing aminocomplex of copper(II)

Procedure. Place 2-3 drops of copper(II) sulphate solution into a test tube and add, drop by drop, 2 *N* ammonia solution to dissolve completely the basic salt $(CuOH)_2SO_4$, that precipitates after addition of the first drops of ammonia solution.

Note the colour of the initial copper sulphate solution and the solution obtained after dissolution of the precipitate.

Recording the results. Write down the equations for the following reactions: (a) between copper(II) sulphate and ammonia solution with formation of the basic copper(II) sulphate; (b) dissolution of the basic copper(II) sulphate in excess ammonia solution with formation of the complex salt and the complex base of copper(II) (the coordination number of Cu^{2+} is 4); (c) dissociation of the obtained complex compounds of copper.

Which base is stronger, copper(II) hydroxide or cupric tetramminohydroxide?

What ions account for the colour of the solution containing amino complexes of copper?

EXPERIMENT 45. SYNTHESIS OF COPPER-ACTIVATED PHOSPHOR

Apparatus and reagents	
Chemical balance. Porcelain dish. Mortar. Porcelain pestle. Graduated cylinders, 10- and 25-ml (or burettes). Drying cabinet.	Muffle furnace. Crucible tongs. Filter paper. Zinc sulphide (for phosphor). Solutions: copper sulphate (containing 4×10^{-4} g Cu^{2+} ions in 1 ml); sodium chloride (containing 4×10^{-2} g NaCl in 1 ml).

Phosphors (also known as luminophores) are substances which can emit light, i.e. luminesce under the influence of external factors, such as the alpha or beta particles, electric current, and the like. Compounds of certain *d* elements, e.g. their sulphides, are phosphors. Electrons of a phosphorescing substance are excited by the energy of external source and then return to the lower energy levels. This process is accompanied with light radiation. Luminescent properties increase when special activators are added. Phosphors are used in the manufacture of luminescent dyestuffs, X-ray screens, TV screens, etc. All phosphors are semiconductors.

Procedure. Synthesize phosphors using 20 g of crystalline zinc sulphide ZnS (fluorescent grade), a solution of copper(II) sulphate containing 4×10^{-4} g/ml of Cu^{2+} ions, and a solution of sodium chloride containing 4×10^{-2} g/ml of NaCl.

Calculate the necessary volumes of copper sulphate and sodium chloride solutions, if 2×10^{-4} g copper should be added per 1 g of ZnS and sodium chloride should make up 2% (by mass) of ZnS.

Weigh out 20 g of zinc sulphide in an accurately weighed porcelain dish. Measure out the necessary volumes of the solutions using the burettes or graduated cylinders (use a separate graduated cylinders for each solution) and transfer them into the porcelain dish with zinc sulphide. Mix thoroughly using a glass rod until a homogeneous paste is obtained. Put the dish in a drying cabinet and cover it with filter paper. Dry at 105-120°C. At ten-minute intervals, remove the disk from the drying cabinet, stir the mass with a glass rod, and triturate with a pestle.

Drying is considered to be over when the substance turns into a powder when it is tapped with a glass rod. Grind the powder in a mortar and transfer into a porcelain crucible by small portions. Compress each portion by tapping the crucible over the bench.

Take the crucible by tongs and put into a hot muffle furnace. Calcine the dust at 750-800°C for 30 minutes, then remove the crucible from the furnace and cool in a desiccator. The sintered bead is phosphor. Check its fluorescence as follows: remove the crust from the surface of the bead without taking it out of the crucible: hold the bead in the sunlight or near an electric bulb for 2-3 minutes. Now transfer the bead to the dark room (or to a box lined with black paper on the inside). Observe the luminescence of the bead which diminishes with time. Expose the material to light again and observe intensification of the luminescence. Check to see that the initial zinc sulphide (not activated with copper) does not luminesce. In other conditions, for example in a spinthariscope whose screen is coated with pure ZnS, scintillation (bright flashes of light) is observed under the exposure to alpha rays. This principle is used in counting alpha particles.

EXPERIMENT 46. SILVER

Apparatus and reagents

Beaker.
Hydrogen sulphide solution. Solutions: sodium hydroxide, 2 *N*; ammonia solution, 2 *N*, 25%; nitric acid, 2 *N*; potassium iodide, 0.1 *N*; sodium thiosulphate, 0.5 *N*; silver nitrate, 0.1 *N*; tin(II) chloride, 0.5 *N*; glucose, 10%; potassium chloride, 0.5 *N*;
potassium bromide, 0.5 *N*; sodium sulphite, 0.5 *N*;
potassium chromate, 0.5 *N*.

Note: All wastes containing silver should be handled over to the laboratory assistant at the end of the experiment.

1. Preparing Silver Oxide

Procedure. Place 3-4 drops of silver nitrate solution into a test tube and add several drops of 2 *N* sodium hydroxide solution to precipitate silver oxide. Save the precipitated Ag_2O for test 3*B*.

Recording the results. Characterize the stability of silver hydroxide. How can the stability of this substance be explained? Write down the equations for the reactions by which silver hydroxide is formed and decomposed.

2. Oxidizing Properties of Silver Oxide

A. Reaction of silver oxide with tin(II) chloride in an alkaline medium

Procedure. Place 2-3 drops of tin(II) chloride solution in a test tube and add, drop after drop, 2 *N* sodium hydroxide solution to dissolve tin(II) hydroxide which first precipitates. Add 1-2 drops of silver

nitrate solution to the obtained alkaline solution of $Na_2[Sn(OH)_4]$. Observe precipitation of black powder of metal silver.

The formation of silver can be proved by adding 5-6 drops of 2 *N* ammonia solution which dissolves silver oxide but does not dissolve silver. Carry out this test.

Recording the results. Write down the equations for the following:

(a) formation of sodium tetrahydroxystannate(II) from tin(II) chloride;

(b) reaction of silver nitrate with alkali;

(c) reaction of sodium tetrahydroxystannate(II) with silver oxide with formation of sodium hexahydroxystannate(IV) and silver metal (water is involved in the reaction);

(d) the overall equation of the reaction between tin(II) chloride and silver oxide in the presence of alkali.

B. Preparing silver mirror

Procedure. Place 25-50 ml of water in a beaker, heat it to boiling, and put the burner aside. Place 4-5 drops of silver nitrate solution into a test tube and add 2-5 drops of 2 *N* ammonia solution. Shake the solution after adding each drop, until Ag_2O, which first precipitates, is dissolved. Avoid adding excess NH_3. Add an equal volume of a 10% glucose solution $C_5H_6(OH)_5CHO$ to the clear solution in the test tube. Mix the solution and put it into the beaker with hot water. In 2-3 minutes, remove the test tube from water, discard the solution from the test tube and rinse it with water from a wash bottle. What substance has deposited on the test tube walls?

Write down the equation for the reaction bearing in mind that glucose converts into gluconic acid $C_5H_6(OH)_5COOH$.

3. Sparingly Soluble and Complex Salts of Silver

A. Preparing amino complexes of silver(I)

Procedure. Place 2 drops of silver nitrate solution into each of four test tubes. Add 2 drops of potassium chloride into one test tube, of potassium bromide into the second, of potassium iodide into the third, and of potassium chromate K_2CrO_4 into the fourth test tube. Note the colour of the precipitates. Add 3 drops of 25% ammonia solution into each test tube. Which precipitates have practically completely dissolved in ammonia? Do the chloride, bromide, and iodide of silver react with ammonia similarly?

Recording the results. Write down the ionic and molecular equations for the following reactions:

(a) formation of sparingly soluble silver salts;

(b) dissolution of the chloride, bromide and chromate of silver in ammonia solution with formation of complex compounds. The coordination number of Ag^+ ion is 2.

Use your observations and solubility products of the silver halides to explain their different solubility in ammonia solution.

B. Preparing complex silver base

Procedure. Add 2 *N* ammonia solution, drop by drop, to the precipitate of silver oxide obtained in test 1. Observe dissolution of the precipitate due to formation of a complex silver base. Write down the equation for the reaction.

C. Preparing complex sulphite and thiosulphate of silver

Procedure. Place silver nitrate solution into a test tube and add sodium thiosulphate $Na_2S_2O_3$ by drops. Observe dissolution of the silver thiosulphate which first precipitates. Carry out a similar experiment with silver nitrate and sodium sulphite.

Recording the results. Write down the equations for the following reactions:

(a) between silver nitrate and sodium thiosulphate with formation of silver thiosulphate, and between silver nitrate and sodium sulphite with precipitation of silver sulphite;

(b) dissolution of the precipitates in excess precipitant, assuming that SO_3^{2-} and $S_2O_3^{2-}$ ions are monodentate, and the coordination number of Ag^+ is 2.

4. (Control Test)

Procedure. Obtain a few drops of a solution from the instructor and test it for the presence of Ag^+ ion. Place the solution into a test tube and add 3-4 drops of 2 *N* hydrochloric acid. The absence of precipitate indicates the absence of Ag^+ ion in the test solution.

If a precipitate falls out, prove that it is a silver salt by carrying out the following reactions specific for Ag^+ ion. Add, drop by drop, 25% ammonia solution to the same test tube to convert the precipitated silver chloride into a complex silver ammoniate. Divide the obtained ammoniacal solution into three portions and place each portion into each of three test tubes. Add a few drops of 2 *N* nitric acid to the first test tube so that the medium becomes acidic (test with litmus paper). Observe precipitation of AgCl. Note that AgCl is insoluble in nitric acid. Add potassium iodide solution to the second test tube. Is the precipitate silver chloride? Add hydrogen sulphide solution to the third test tube. What is the black substance that precipitates?

Recording the results. Describe your observations. Write down the equations for the following reactions:

(a) preparing silver chloride and its dissolution in ammonium hydroxide;

(b) reaction of diamminesilver chloride with nitric acid, taking into account that the complex NH_4 ion is formed, which is more stable than the silver-ammonium complex;

(c) reaction between diamminesilver chloride and potassium iodide taking into account that unlike silver chloride, silver iodide is insoluble in ammonia solution because of its low solubility product;

(d) reaction of diamminesilver chloride with hydrogen sulphide water with formation of a very sparingly soluble silver sulphide Ag_2S.

19 Elements of Subgroup VIIIB

QUESTIONS AND PROBLEMS

1. Write down the electron formulas of iron, cobalt, and nickel atoms.
2. Which of the ions, Fe^{2+}, Co^{2+}, or Ni^{2+} has stronger oxidizing properties? Illustrate your answer by equations of reactions in which this difference is demonstrated.
3. Is Fe^{3+} ion an oxidant or reductant in chemical reactions? Give examples of reactions to prove your answer. Write down the equations for these reactions.
4. Write down the equations for two reactions by which Fe^{2+} can be differentiated from Fe^{3+} in a solution.
5. How can (a) iron(II) salt, and (b) iron(III) salt be prepared from iron? Write down the reaction equations.
6. Write down the formulas of two iron(III) salts in one of which iron is the cation and in the other it is a part of an anion.
7. Write down the equation for the reaction between iron(III) chloride and alkali (in a melt and in a solution)
8. When preparing aqueous solutions of iron(III) salts acid is added. Explain.
9. What reactions occur in a mixture of iron(II) and iron(III) salt solutions if hydrogen sulphide water or ammonium sulphide is added? Write down the equations for these reactions.
10. Write down the formulas for complex compounds of iron, potassium ferrocyanide and potassium ferricyanide, and explain distribution of electrons of the iron atom between the quantum cells during formation of the complexes. Which of these compounds is paramagnetic?
11. How can iron(II) salt be converted into iron(III) salt? How can the back conversion be realized? Write down the equations for the corresponding reactions.
12. Can the following substances exist simultaneously in a solution?
(a) $Fe(OH)_2$ and H_2O_2: (b) $Ni(OH)_2$ and H_2O_2:
(c) $Co(OH)_2$ and H_2O_2: (d) $FeCl_3$ and H_2S
13. Which of the metals, cadmium or nickel, is a better protector of iron from corrosion? Explain your answer.

14. To which oxidation states is iron oxidized by
(a) dilute and concentrated sulphuric acid;
(b) dilute and concentrated hydrochloric acid;
(c) dilute nitric acid?
Write down the equations of the corresponding reactions.
15. Which complex salt of cobalt is more stable, $[Co(NH_3)_6]Cl_2$ or $[Co(NH_3)_6]Cl_3$? Reason your answer and consult Table 12 of Appendix to see if this agrees with the instability constant of the corresponding complex ions.
16. Write down the equation for the reaction between cobalt(III) hydroxide and concentrated hydrochloric acid. What gas is liberated during this reaction?
17. Write down the formulas for the following complex salts of nickel; hexamminenickel chloride and hexacyanonickel chloride. Distribute the nickel atom electrons between the quantum cells in these complexes. Which of these compounds is paramagnetic? What is the configuration of these complexes?
18. To a solution of the complex salt $[Ni(NH_3)_6]Cl_2$ added were the following; (a) NaOH solution; (b) hydrogen sulphide. Write down the equations for the corresponding reactions. Find solubility products for the nickel compounds prepared by these reactions and decide in which case the complex ion will be destroyed more completely.
19. Complete the following equations:

(a) $Co(OH)_2 + H_2SO_4 \rightarrow CoSO_4 + \ldots$
(b) $Co(OH)_3 + HCl$ (conc.) $\rightarrow$

20. The oxidation-reduction potentials for the conversion of cobalt(II) complex ion into cobalt(III) complex ion are the following;

$[Co(H_2O)_6]^{2+} = [Co(H_2O)_6]^{3+} + e^-$ $\quad \varphi^\circ = 1.84$ V
$[Co(NH_3)_6]^{2+} = [Co(NH_3)_6]^{3+} + e^-$ $\quad \varphi^\circ = 0.1$ V

How can the easy oxidability of the cobalt(II) ammino complex (compared with that of its aquo complex) be explained?
21. Write down the equation of the reaction by which iron(III) chloride is oxidized with bromine in an alkaline medium to K_2FeO_4.

Examples of Multiple-choice Questions

1. Which salt, formed by Fe^{3+} cation and the anions of the acids given below, is readily soluble in water?
(1) H_3PO_4; (2) HSCN; (3) H_2SiO_3; (4) HCl; (5) H_2CO_3.
2. What substances are formed by the reaction of nickel(III) hydroxide with concentrated hydrochloric acid?
(1) $NiCl_3$, H_2O; (2) $NiCl_2$, Cl_2O, H_2O; (3) $NiCl_2$, H_2O, Cl_2; (4) $NiCl_2$, Cl_2O, H_2; (5) $NiCl_3$, Cl_2, H_2O.
3. Complete the following equation:

$FeSO_4 + KIO_3 + H_2SO_4 = I_2 + \ldots$

What is the sum of the coefficients in the right side of the equation?
(1) 15; (2) 8; (3) 11; (4) 13; (5) 5.
4. Which of the hydroxides is the strongest oxidant?
(1) $Fe(OH)_2$; (2) $Co(OH)_3$; (3) FeOOH; (4) $Co(OH)_2$; (5) $Ni(OH)_3$.
5. In which of the following reactions iron(III) compound acts as a reductant?

(1) $FeOOH + KI =$
(2) $FeCl_3 + H_2S =$
(3) $FeOOH + KOH$(conc.) $=$
(4) $FeCl_3 + Br_2 + NaOH =$
(5) $Fe_2(SO_4)_3 + NaOH =$

EXPERIMENT 47. IRON

Apparatus and reagents

Forceps. Clay triangle.
Crucible. Iron shavings.
Iron(II) oxalate. Mohr's salt.
Iron(III) nitrate. Sodium sulphate.
Zinc, granules. Potassium hydroxide.
Bromine. Hydrogen sulphide solution.
Litmus, neutral solution. Solutions:
hydrochloric acid, 2 *N*;
sulphuric acid,
2 *N*, density 1.84 g/cm^3; nitric acid,
2 *N*, density 1.4 g/cm^3; potassium (or ammonium) thiocyanate, 0.01 *N*;
sodium hydroxide, 2 *N*;
sodium carbonate, 0.5 *N*;
ammonium sulphide, 0.5 *N*;
potassium ferrocyanide, 0.5 *N*;
potassium ferricyanide, 0.5 *N*;
hydrogen peroxide, 3%; silver nitrate,
0.1 *N*; iron(III) chloride, 0.5 *N*,
saturated; potassium iodide, 0.5 *N*;
barium chloride, 0.5 *N*;
orthophosphoric acid, 2 *N*;
hydrofluoric acid, 2 *N*.

1. Preparing Pyrophoric Iron

Certain substances, e.g. Fe, Co, Ni, rare earth elements, can spontaneously ignite in the air at room temperature when crushed to fine particles. These substances are called pyrophores.

Procedure. Place powdered iron oxalate FeC_2O_4 into a test tube to 1/4 its capacity and fix the tube in the horizontal position in the stand. Heat the test tube over a burner until the yellow powder turns black and evolution of gas discontinues. Put the burner aside and quickly close the test tube with a stopper so that the obtained iron is not oxidized with atmospheric oxygen. Allow the test tube to cool and spill the reduced iron from the test tube onto a sheet of paper from the height of 25-30 cm.

Recording the results. Describe your observations. Write down the equations for the reactions of (a) iron oxalate decomposition, and (b) burning of iron (the product of iron burning is the oxide Fe_3O_4).

2. Specific Reactions for Fe^{2+} and Fe^{3+} Ions

A. Effect of potassium ferricyanide on iron(II) salts

Procedure. Prepare a solution of Mohr's salt in a test tube and add a drop of potassium ferricyanide solution (red Prussiate $K_3[Fe(CN)_6]$). Note the colour of the precipitate (Turnbull's blue), name the compound, and write down its chemical formula. The reaction is specific for Fe^{2+} ion.

Write down the ionic and molecular equations for the reaction.*

* It has been recently established that the molecules of Berlin and Turnbull blues have identical structures, the difference in their hues depending on the different ratio of Fe^{2+} and Fe^{3+} atoms.

B. Action of potassium ferrocyanide on iron(III) salts

Procedure. Place 2-3 drops of iron(III) chloride solution in a test tube and add a drop of potassium ferrocyanide solution (yellow Prussiate, $K_4[Fe(CN)_6]$). Observe the reaction.

Recording the results. Note the colour of the precipitate (Berlin blue), give its chemical name, and write down the formula. Write down the ionic and molecular equations for the reaction (see footnote on p. 215).

C. Action of potassium (or ammonium) thiocyanide on iron(III) salts

Procedure. Place 5-6 drops of iron(III) chloride solution into a test tube and add a drop of a 0.01 *N* potassium (or ammonium) thiocyanate solution. Conduct a similar experiment using a Mohr's salt solution. Transfer a drop of the solution obtained in the first test tube into another test tube and add 8-10 drops of water.

Recording the results. Write down the equation for the reaction by which $Fe(SCN)_3$ is prepared.* The presence of this salt accounts for the bright red colour of the solution, which is specific for iron(III) salts. Explain fading of the colour with dilution.

3. Reaction of Iron with Acids

Procedure. Place 5 drops of 2 *N* solutions of the following acids: hydrochloric into the first test tube, sulphuric acid into the second, and nitric acid into the third test tube. Place 3 drops of concentrated sulphuric acid (density 1.84 g/cm^3) into the fourth test tube. Add small quantity of iron shavings or chips into each test tube. Heat carefully the test tube containing concentrated sulphuric acid and iron. Observe the reactions. Add a drop of 0.01 *N* potassium (or ammonium) thiocyanate solution into each test tube: the solutions acquire red colour specific for $Fe(SCN)_3$.

Make sure that Fe^{2+} ions are formed in hydrochloric and dilute sulphuric acid, while Fe^{3+} ions are formed in nitric acid and concentrated sulphuric acid. Observe the colour of the solutions attentively, because $Fe(SCN)_3$ decomposes in an acidic medium in 1-2 minutes.

Recording the results. Write down the equations for the reactions performed. Which ions act as oxidants in each reaction? Explain why iron reacts with dilute and concentrated sulphuric acid to give salts of iron in different oxidation states.

4. Iron(II) Hydroxide

Iron(II) salts always contain iron in the oxidation state(III) because of partial oxidation in air. The stable salt of iron, Mohr's

* Several complex ions. from $[Fe(SCN)_2]^+$ to $[Fe(SCN)_6]^{3-}$ are actually formed during this reaction.

double salt $(NH_4)_2SO_4 \cdot FeSO_4 \cdot 6H_2O$, should therefore be used in experiments to study the properties of iron(II). In order to prepare a solution of this salt, place two microspatulas of the salt into a test tube and dissolve in 4-5 drops of water. Explain the high stability of Mohr's salt in the crystal state (compared with iron(II) sulphate). Why should the solution of $(NH_4)_2SO_4 \cdot FeSO_4 \cdot 6H_2O$ be prepared immediately before the experiment? Write down the coordination formula of Mohr's salt.

When writing down reaction equations, the formula of iron(II) sulphate can be substituted for Mohr's salt formula because the double salt almost completely dissociates during dissolution in water and falls into its component ions.

Procedure. Place 3-4 drops of Mohr's salt solution into a test tube and add 2 *N* alkali solution until a green iron(II) hydroxide precipitates. Stir the precipitate using a glass rod and observe oxidation of iron(II) hydroxide to iron(III) hydroxide FeOOH: the green precipitate turns brown.

Carry out a reaction between freshly precipitated iron(II) hydroxide and 2 *N* hydrochloric acid. What properties of iron(II) hydroxide are demonstrated in this reaction?

Recording the results. Write down the equations for the reactions of (a) formation of iron(II) hydroxide; (b) oxidation of the obtained base to iron(III) hydroxide by oxygen of the air and water.

5. Reducing Properties of Iron(II) Compounds

A. Reduction of nitric acid

Procedure. Prepare Mohr's salt solution in each of two cylindrical test tubes. Add a drop of concentrated nitric acid (density 1.4 g/cm^3) into one test tube and heat the solution until gas stops evolving. Allow the solution to cool. Add a drop of 0.01 *N* ammonium thiocyanate solution to both test tubes. In which test tube does the solution turn red? Why? Write down the equation for the reaction, assuming that nitric acid is mostly reduced to NO.

B. Reduction of hydrogen peroxide

Procedure. Prepare Mohr's salt solution in each of two test tubes. Add 2-3 drops of 2 *N* sulphuric acid into one test tube and the same amount of a 3% solution of hydrogen peroxide to the other. Add a drop of 0.01 *N* ammonium thiocyanate solution to both test tubes. The solution turns red in which test tube? Why?

Check experimentally how the reduction of hydrogen peroxide with iron(II) salt proceeds in an alkaline medium. Observe precipitation of iron(III) hydroxide. Write down the equations for the reactions.

C. Reduction of silver nitrate

Procedure. Prepare Mohr's salt solution in each of two test tubes. Add 6-7 drops of silver nitrate solution to the first test tube and heat slightly over a low flame of the burner without boiling the solution. Observe the deposition of silver mirror on the walls of the test tube. What reaction occurs in this test tube?

Cool the test tube and add a drop of 0.01 *N* ammonium thiocyanate solution to it and to the second test tube. The solution is coloured in which test tube? Why?

Write down the equation for reduction of silver nitrate with iron(II) salt:

$3AgNO_3 + 3FeSO_4 = 3Ag + Fe(NO_3)_3 + Fe_2(SO_4)_3$

6. Iron(III) Hydroxide

Procedure. Place 5-6 drops of iron(III) chloride solution into each of two test tubes and add 3-4 drops of 2 *N* alkali solution to both. Observe the reaction. Add dilute acid to one test tube to dissolve the precipitate. Test the precipitate in the second test tube for solubility in alkali.

Iron(III) hydroxide does not react with alkali under ordinary conditions, but nevertheless, it is weakly amphoteric. Its acidic properties are only demonstrated during fusion with alkali or carbonates of the alkali metals. This reaction gives salts of ferrous acid, the ferrites, which are completely hydrolyzed in water.

Recording the results. Write down the equations for the reactions of (a) iron(III) chloride with alkali solution to form iron(III) hydroxide $Fe(OH)_3$*; (b) dissolution of iron(III) hydroxide in acid; (c) formation of ferrites during fusion; complete the following:

$Fe_2O_3 + Na_2CO_3 \rightarrow$
$Fe_2O_3 + KOH \rightarrow$

(d) complete hydrolysis of sodium ferrite with formation of FeOOH; (e) write down the formula of the oxide Fe_3O_4 in the form of iron ferrite.

7. Oxidizing Properties of Iron(III) Compounds

A. Oxidation of potassium iodide

Procedure. Place 3-4 drops of $FeCl_3$ solution into a test tube and add 1-2 drops of potassium iodide solution. Observe the colour change and explain this. Write down the reaction equation.

* The existence of $Fe(OH)_3$ has not yet been proved experimentally. A more correct formula of iron(III) hydroxide is $Fe_2O_3 \cdot nH_2O$. Part of the precipitate is possibly FeOOH.

B. Oxidation of sodium sulphite

Procedure. Place 3-4 drops of iron(III) chloride solution into a test tube and add a few crystals of sodium sulphite. The solution first colours brown-red due to formation of an unstable iron(III) sulphite. The colour vanishes when the test tube is heated.

Make sure that the iron has reduced to its oxidation state of +II. What reagent should be used to prove this?

Write down the equation for oxidation of sodium sulphite with iron(III) chloride. Mind that water is involved in the reaction.

8. Hydrolysis of Iron Salts

A. Hydrolysis of iron(II) sulphate

Procedure. Place 5-6 drops of neutral litmus solution into a test tube and add two microspatulas of Mohr's salt. Stir the solution using a glass rod. Establish the reaction of the medium by the colour of litmus.

Write down the equation for the hydrolysis of $FeSO_4$.

B. Hydrolysis of iron(III) chloride

Procedure. Place 5-6 drops of neutral litmus solution into each of two test tubes and add two microspatulas of iron(III) chloride to each test tube. Determine the reaction of the medium by the colour of litmus. Heat one test tube and observe the reaction.

Recording the results. Write down the equation for hydrolysis of $FeCl_3$ in the cold and with heating. How can the degree of hydrolysis of this salt be decreased? Which salt, $FeCl_2$ or $FeCl_3$, is hydrolyzed stronger? Explain your answer.

C. Hydrolysis of iron(III) chloride in the presence of soda

Procedure. Place 3-4 drops of iron(III) chloride solution into a test tube and add, drop by drop, a soda solution. Observe precipitation of FeOOH. What gas is evolved? Write down the equation for the reaction.

9. Action of Hydrogen Sulphide and Ammonium Sulphide on Iron(II) and Iron(III) Salts

A. Iron(II) salts

Procedure. Place 5-6 drops of freshly prepared Mohr's salt solution into each of two test tubes and add 2 drops of hydrogen sulphide solution into one, and of ammonium sulphide into the other test tube. In which of the test tubes does iron(II) sulphide precipitate? Test the precipitate for solubility in dilute hydrochloric acid.

Recording the results. Explain why iron(II) sulphide is not precipitated by the action of hydrogen sulphide solution, but is precipitated by ammonium sulphide. Write down the ionic and molecular equations for the reactions of formation of iron(II) sulphide and its dissolution in hydrochloric acid.

B. Iron(III) salts

Procedure. Place 3-4 drops of iron(III) salt solution into each of two test tubes. Add 2 drops of hydrogen sulphide solution into one and the same amount of ammonium sulphide into the other test tube. Are the precipitates of the same colour?

Recording the results. Answer the following questions:

(a) Why do hydrogen sulphide and ammonium sulphide not precipitate iron(III) sulphide from iron(III) salts?

(b) What property of iron(III) accounts for the precipitation of colloidal sulphur in both test tubes?

(c) Bearing in mind that the initial solution of iron(III) salt is acidified (to decrease hydrolysis), explain why ammonium sulphide precipitates iron(II) sulphide.

Write down the equations for all these reactions.

10. Iron(VI) Compounds

Procedure. Place a few grains of crushed potassium hydroxide into a test tube using forceps. Add a drop of a saturated iron(III) chloride solution(*in the hood*) and 2 drops of bromine. Heat slightly the solution. A violet solution of a potassium salt of ferric acid, potassium ferrate (K_2FeO_4), is formed. Using a microspatula, transfer a small quantity of the prepared substance into another test tube containing 3-4 drops of barium chloride solution and observe precipitation of barium ferrate.

Recording the results. Write down the equations for the following reactions:

(a) oxidation of iron(III) chloride with bromine in an alkaline medium;

(b) formation of sparingly soluble barium ferrate;

(c) decomposition of a salt containing ferrate ion in an acidic medium according to the scheme

$$FeO_4^{2-} + H^+ \rightarrow Fe^{3+} + O_2 + H_2O$$

if it is known that the ferrate ion is stable only in an alkaline solution.

11. Complex Compounds of Iron

A. Preparing complex iron(III) phosphate

Procedure. Place 3-4 drops of iron(III) chloride solution into a test tube and add a drop of a 0.01 *N* solution of ammonium thiocyanate and then two drops of 2 *N* orthophosphoric acid solution. Observe the reaction. Bearing in mind that the stable complex ion $[Fe(PO_4)_2]^{3-}$ is colourless, explain the observed phenomenon and write down the corresponding reaction.

B. Preparing complex iron(III) fluoride

Procedure. Place 3-4 drops of iron(III) chloride solution into a test tube and add a drop of 0.01 *N* ammonium thiocyanate and two drops of 2 *N* hydrofluoric acid solutions. Observe the reaction. Bearing in mind that the complex ion $[FeF_6]^{3-}$ is colourless, explain the observed phenomenon and write down the equation for the corresponding reactions.

EXPERIMENT 48. SYNTHESIS OF MOHR'S SALT

Apparatus and reagents

Three beakers, 100-ml. Büchner funnel. Water bath. Burette, 25-ml. Pipette, 10-15-ml. Three conical flasks, 50-ml.

Reduced iron. Ammonium sulphate. Sulphuric acid, 10% solution. Potassium permanganate, 0.1 *N* standard solution.

Procedure. Mohr's salt is crystallized from solutions containing iron(II) sulphate and ammonium sulphate.

Prepare a solution of iron(II) sulphate. To do so, weigh out 2 g of reduced iron on a chemical balance and dissolve in a beaker in a 10% solution of sulphuric acid with heating. (Calculate preliminarily the necessary volume of the acid by the reaction equation; find its density in Table 4 of Appendix). Separate the hot solution from carbon by filtration and keep the solution in a water bath until a film is formed on the surface. Now, prepare a saturated solution of ammonium sulphate. Calculate the necessary amount of the crystalline salt and dissolve it in water by adding the latter in small portions to the salt until the crystals dissolve completely. Evaporate the obtained solution in a water bath till crystallization begins. Pour together both hot solutions and keep in a water bath until a crystalline film is formed on the surface. Allow the mixture to stand for 24 hours

for crystallization at room temperature. The formed double salt precipitates in the form of bluish green crystals:

$$FeSO_4 + (NH_4)_2SO_4 + 6H_2O = (NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$$

Separate the crystals on a Büchner funnel, rinse them with 10 ml of ice-cold water, and dry between filter papers.

1. Weigh the salt and calculate the yield with respect to iron (in %).
2. Carry out the known reactions to determine the oxidation state of iron in the obtained salt.
3. Determine the quantity of iron in the prepared salt. To do so, dissolve 0.1 g of the salt in a 100-ml volumetric flask, add water to the mark, and titrate with potassium permanganate prepared from the standard solution (see Experiment 19, test 2). Compare your result with the theoretical content of iron in Mohr's salt.

EXPERIMENT 49. COBALT. NICKEL

Apparatus and reagents

Clay triangle.
Crucible. Glass tube. Cobalt, shavings. Nickel, shavings.
Cobalt(II) nitrate.
Nickel(II) nitrate.
Calcium chloride. Nickel(II) chloride.
Potassium nitrite. Bromine water.
Ethyl alcohol. Dimethylglyoxime, ammonia water-alcohol solution.
Solutions:
hydrochloric acid, 2 *N*, density 1.19 g/cm^3; sulphuric acid, 2 *N*; nitric acid, 2 *N*; cobalt nitrate, 0.02 *N*, 0.5 *N* and saturated; cobalt chloride, 0.5 *N*; sodium hydroxide, 2 *N*;
hydrogen peroxide, 3% solution;
nickel nitrate, 0.5 *N*; ammonium sulphide, 0.5 *N*; ammonium thiocyanate, saturated; ammonia solution, 25%.

1. Reaction of Cobalt and Nickel with Acids

A. Reaction of cobalt with acids

Procedure. Place a piece of cobalt shaving into each of three test tubes. Add 4-5 drops of 2 *N* hydrochloric acid solution to the first test tube, of 2 *N* sulphuric acid to the second, and 2-3 drops of 2 *N* nitric acid to the third test tube. Heat slightly the test tubes and observe evolution of gas. What are these gases? What is the colour of the solutions? Write down the equations for the reactions.

B. Reaction of nickel with acids

Procedure. Place a small piece of nickel shaving into each of three test tubes and add 4-5 drops of 2 *N* hydrochloric acid to the first test tube, the same amount of 2 *N* sulphuric acid to the second, and

2-3 drops of 2 *N* nitric acid solution to the third test tube. Heat the test tubes slightly and observe evolution of gases. What are these gases? What is the colour of the solutions? Write down the equations for the reactions.

2. Cobalt and Nickel Oxides

A. Preparing cobalt(III) oxide

Procedure. Place a few crystals of cobalt(II) nitrate into a crucible, put it into a clay triangle over the burner and heat over a low flame until gas evolution stops.

Cool the crucible, transfer its contents into the test tube and add 2-3 drops of concentrated hydrochloric acid (density 1.19 g/cm^3). Identify the gas by its odour.

Recording the results. Cobalt(II) nitrate decomposes according to the following equation

$$4Co(NO_3)_2 = 2Co_2O_3 + 8NO_2 + O_2$$

Indicate the oxidant and reductant in this reaction. Write down the equation for the reaction between cobalt(III) oxide and concentrated hydrochloric acid.

What properties of cobalt(III) oxide are demonstrated by this reaction? What is the colour of the obtained solution?

B. Preparing nickel oxides

Procedure. Fix a glass tube in the stand in the horizontal position and place two microspatulas of nickel(II) nitrate into it. Heat the tube where the salt is with a small flame of the burner. Observe formation of black nickel(III) oxide and make sure that oxygen evolves by putting a glowing splint into the gas. Continue heating the unstable nickel(III) oxide until it converts into the stable greyish-green nickel(II) oxide. Allow the tube to cool, discharge its contents onto a sheet of paper, and transfer a few grains of the oxide into a test tube. Add 2-3 drops of 2 *N* HCl solution and heat slightly. What is observed?

Recording the results. Describe the test done. Write down the equations for the following reactions:

(a) thermal decomposition of nickel(II) nitrate with formation of nickel(III) oxide:

(b) conversion of nickel(III) oxide into nickel(II) oxide.

3. Hydroxides of Cobalt(II) and Nickel(II)

A. Preparing cobalt(II) hydroxide and its oxidation

Procedure. Place 2-3 drops of a cobalt salt into each of two test tubes and add, drop after drop, sodium hydroxide solution to both. A blue basic salt first precipitates, which then turns pink to indicate formation of cobalt(II) hydroxide. Stir thoroughly the precipitate in one test tube using a glass rod, and add 2-3 drops of a 3% solution of hydrogen peroxide to the other. In which test tube is cobalt(II) hydroxide oxidized?

Recording the results. Write down the equations for the reactions. Compare your findings with the results of the experiment where iron(II) hydroxide is oxidized (see Experiment 47, test 4). Which ion is a stronger reductant, Co^{2+} or Fe^{2+}?

B. Preparing nickel(II) hydroxide and its oxidation

Procedure. Place 2-3 drops of a nickel salt into each of three test tubes. Add an alkali solution by drops to all test tubes until nickel(II) hydroxide precipitates. Stir thoroughly the precipitate in the first test tube using a glass rod, and add 2-3 drops of a 3% solution of hydrogen peroxide to the second solution. Does the colour of the precipitate change? Is nickel(II) hydroxide oxidized with atmospheric oxygen and hydrogen peroxide? Add a drop of bromine water to the third test tube. What is observed?

Recording the results. Answer the questions. Write down the equations for the reactions. Compare the reducing properties of hydroxides of iron, nickel, and cobalt in the oxidation state +II, using your own observations and by comparing their standard oxidation-reduction potentials (during conversion to the hydroxides with oxidation state +III).

4. Complex Compounds of Nickel and Cobalt

A. Aqua complex of cobalt(II) and its decomposition

Procedure. Place 4-5 drops of a saturated solution of cobalt(II) salt into each of two test tubes. Add 2 drops of concentrated hydrochloric acid (density 1.19 g/cm^3) to one test tube, and a piece of calcined calcium chloride to the other test tube. Observe the reaction.

Place a microspatula of a cobalt salt into the third test tube and add 3-4 drops of ethyl alcohol. Note the colour of the obtained solution. Add 7-8 drops of water until the colour changes again.

Dip a glass rod in 0.02 *N* $CoCl_2$ solution and write some characters on filter paper. Dry the paper and then heat slightly over a flame of

the burner: the characters become visible. Note vanishing of the characters on cooling.

Recording the results. Describe the observed phenomena. The change in the colour of the solution in all cases is explained by the fact that the unstable complex $[Co(H_2O)_6]^{2+}$ colours the solution pink, while Co^{2+} ion accounts for the blue colour.

B. Preparing complex cobalt thiocyanate

Procedure. Place 2 drops of a saturated cobalt(II) salt solution into a test tube and add 5-6 drops of a saturated ammonium thiocyanate solution. The solution of a complex salt $(NH_4)_2[Co(SCN)_4]$ is formed. The complex ion $[Co(SCN)_4]^{2-}$ is blue, while the hydrated ion $[Co(H_2O)_6]^{2+}$ is pink. Note the colour of the obtained solution. Dilute it with water until the colour changes, add 2 drops of an ether-alcohol mixture, stir the solution using a glass rod, and observe again the colour change. Add distilled water to the same test tube and observe a gradual colour change.

Recording the results. Describe the observed phenomena. Write down the following:

(a) equation for dissociation of the cobalt complex salt;
(b) equation for dissociation of the complex ion;
(c) instability constant of the complex ion.

How do water and alcohol shift the equilibrium during dissociation of the complex ion?

C. Preparing ammino complexes of cobalt

Procedure. Place 3-4 drops of a cobalt(II) salt solution into a test tube and add, drop after drop, a 25% solution of ammonia to precipitate cobalt(II) hydroxide. As the ammonia solution is further added, the cobalt(II) hydroxide is dissolved to convert into a complex compound in which the cobalt has the coordination number of 6. Transfer the obtained solution into two test tubes. Stir the solution in one test tube thoroughly using a glass rod until the colour changes due to oxidation of the obtained complex compound of cobalt(II) to a complex compound of cobalt(III). Why is the ammino complex ion of Co(II) oxidized by atmospheric oxygen, while the aqua complex of Co(II) can only be oxidized by hydrogen peroxide? Add 2-3 drops of 3% hydrogen peroxide solution to the second test tube. Explain the colour change. Add 2-3 drops of ammonium sulphide solution to both test tubes: a precipitate falls out. Explain.

Recording the results. Write down the equations for the following reactions:

(a) formation of ammino complex of cobalt(II);

(b) its oxidation with atmospheric oxygen and hydrogen peroxide to the ammino complex of cobalt(III);

(c) dissociation of the obtained complex compounds;

(d) dissociation of the complex ions. Write down the instability constants for the complex ions. Which ion is more stable? Explain your answer;

(e) interaction of the ammino complex of cobalt(III) with ammonium sulphide.

Compare the coordination formulas of the complex compounds of cobalt in its various oxidation states. Do their spatial configurations differ?

D. Preparing nitrite complex of cobalt

Procedure. Place 3-4 drops of a saturated cobalt(II) salt solution into a test tube and add a microspatula of potassium nitrite crystals. Add 1-2 drops of a 2 *N* solution of sulphuric acid. What gas is liberated? Observe precipitation in a few minutes. Note the colour of the precipitate.

Recording the results. Write down the equations for the reactions taking into account that potassium nitrite oxidizes cobalt(II) to cobalt(III) in the presence of sulphuric acid; an insoluble complex compound $K_3[Co(NO_2)_6]$ is thus formed. Name the obtained complex compound.

E. Preparing ammino complex of nickel

Procedure. Place a microspatula of cobalt(II) salt in a test tube and dissolve it in 5 drops of water. Add 5 drops of 25% ammonia solution. How does the colour of the solution change? Add 2-3 drops of ammonium sulphide solution. What substance is precipitated?

Recording the results. Write down the equations for the following:

(a) reaction of formation of ammino complex of nickel (the coordination number of nickel is 6);

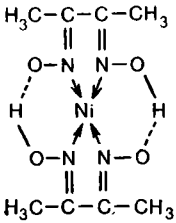
(b) dissociation of the complex compound and of the complex ion;

(c) reaction of the obtained complex compound of nickel with ammonium sulphide. Explain the reaction mechanism using the instability constant of the complex ion and the solubility product.

5. Dimethylglyoxime, the Reagent for Nickel Ion (Chugaev's Reaction)

Procedure. Place 5-6 drops of water in a test tube and add 2 drops of a nickel salt and a drop of dimethylglyoxime solution in ammonia. The reaction proceeds with formation of an insoluble complex nickel dimethylglyoximate. It is a chelate compound with the follow-

ing structural formula



(the hydrogen bonds are shown by dashes).

The colour of the precipitate is intense and bright, which makes it possible to use this reaction to detect minute quantities of nickel ions in a solution.

EXPERIMENT 50. SYNTHESIS OF HEXAMMINENICKEL(II) CHLORIDE

Apparatus and reagents

Two beakers, 100-ml.
Büchner funnel. Crystallizer.
Graduated cylinder, 100-ml.
Nickel chloride.
Ammonium chloride.
Ammonia,
25% solution.
Ethyl alcohol. Ethyl ether.

Procedure. Weigh out 5 g of nickel chloride on a chemical balance and dissolve it in the minimum quantity of water. Add 30-35 ml of concentrated ammonia solution. Take separately 10 ml of a saturated ammonium chloride solution, add 3 ml of concentrated ammonia solution to it. Pour the prepared solution into the solution of nickel chloride. This is necessary to ensure complete precipitation of hexamminenickel(II) chloride. Allow the solution to stand for 20 minutes and transfer it onto a Büchner funnel and filtrate. Wash the precipitate on the filter with 10-15 ml of concentrated ammonia solution, then with 10 ml of alcohol (in small portions), and finally with ether.

Dry the blue-violet crystals of hexamminenickel(II) chloride in a drying cabinet at a temperature not above 100°C, weigh the salt and calculate its yield with respect to nickel chloride. Examine the crystals of $[Ni(NH_3)_6]Cl_2$ under a microscope. Draw sketches of the crystals.

20 Elements of Subgroup VIIB

QUESTIONS AND PROBLEMS

1. Indicate similarity and differences in the structure of the atoms of the elements in subgroups VIIA and VIIB using chlorine and manganese as examples. How do these differences influence the properties of the elements and of their oxides and hydroxides?
2. Write down the formulas of possible oxides of manganese and the corresponding hydroxides. Indicate their properties: acidic, basic, or amphoteric.
3. Write down the electron formulas of Mn(IV) and Mn(VII), Re(III) and Re(VII). Which of these atoms in the mentioned oxidation state is the strongest oxidant? Which is the strongest reductant?
4. What acids can dissolve manganese? Rhenium? Write down the equations for the corresponding reactions.
5. The most stable rhenium oxides are Re_2O_7, ReO_3, and ReO_2. What substances will be formed when these oxides are fused with NaOH (a) in air, and (b) in the absence of oxidant?
6. Added to a manganese sulphate solution were (a) potassium hydroxide; (b) ammonium sulphide; (c) potassium permanganate. What manganese compound is obtained in each of these cases? Write down the equations for the corresponding reactions.
7. Write down the equations for the reactions in which manganese(II) sulphate is used to prepare (a) manganese(III) hydroxide; (b) manganese dioxide; (c) permanganic acid.
8. Write down the equations for the reactions in which manganese(IV) compound acts as (a) reductant; (b) oxidant.
9. Write down the equations for the reactions between manganese dioxide and (a) concentrated hydrochloric acid; (b) concentrated sulphuric acid.
10. Write down the equations for two reactions by which manganates are obtained by (a) oxidation; (b) reduction of the corresponding manganese compounds.
11. Write down the molecular equations for the reactions by which the following conversions are realized:
(a) $MnO_4^- \rightarrow Mn^{2+}$; (b) $MnO_4^- \rightarrow MnO_2$; (c) $Mn^{2+} \rightarrow MnO_4^-$.
12. What reactions occur when (a) concentrated sulphuric acid, (b) concentrated hydrochloric acid act on crystalline potassium permanganate? What reaction occurs during heating of the crystals?
Write down the equations for the corresponding reactions.
13. Consult the Table of electrode potentials and write down the molecular equation for a possible reaction of oxidation with permanganate:

(a) $MnO_4^- + Cr^{3+} + H^+ \rightarrow Mn^{2+} + Cr_2O_7^{2-} + \ldots$

(b) $MnO_4^- + Bi^{3+} + H^+ \rightarrow Mn^{2+} + BiO_3^- + \ldots$

Examples of Multiple-choice Questions

1. Indicate the number of electrons in the level $n = 3$ of the manganese atom:
(1) 7; (2) 10; (3) 8; (4) 13; (5) 18.
2. The reaction $KMnO_4 + K_2S + \ldots \rightarrow MnO_4^{2-} + S + \ldots$ is possible at which pH?
(1) 3; (2) 7; (3) 6; (4) 12; (5) 2.
3. Determine the coefficient at sulphuric acid in the following reaction
$KMnO_4 + CaS + H_2SO_4 = MnSO_4 + CaSO_4 + S + H_2O + K_2SO_4$
(1) 4; (2) 8; (3) 16; (4) 24; (5) 36.

4. Indicate an oxidant that can oxidize Mn^{2+} to MnO_4^-
(1) $K_2Cr_2O_7$; (2) H_2SO_4; (3) $NaBiO_3$; (4) Cl_2; (5) KIO_3.
5. Indicate the substances that are produced during thermal decomposition of potassium permanganate:
(1) K_2O, MnO_2, O_2; (2) K_2MnO_3, O_2; (3) K_2MnO_4, MnO_2, O_2; (4) K_2O, Mn_2O_7; (5) MnO_3, K_2MnO_4.

EXPERIMENT 51. MANGANESE. RHENIUM

Apparatus and reagents

Ring stand.
Asbestos-centred gauze. Porcelain crucible. Clay triangle. Forceps. Pipette. Splint. Filter paper. Manganese, solid or powder. Glass rods.
Sodium hydroxide. Potassium (or sodium) nitrate. Potassium permanganate. Sodium sulphite. Mohr's salt. Sodium bismuthate. Manganese dioxide. Lead dioxide. Ammonium peroxydisulphate. Litmus paper, blue. Ethyl alcohol. Solutions: bromine water; chlorine water; sodium hydroxide, 2 *N*; hydrochloric acid, 2 *N*, density 1.19 g/cm³; sulphuric acid, 2 *N*, density 1.84 g/cm³; nitric acid, 2*N*; acetic acid, 2 *N*; manganese sulphate, 0.5 *N*; potassium chromate, 0.5 *N*; ammonium carbonate, 0.5 *N*; ammonium sulphide, 0.5 *N*; potassium iodide, 0.1 *N*; potassium permanganate, 0.5 *N*; hydrogen peroxide, 10% solution; silver nitrate, 0.1 *N*; ammonium perrhenate, saturated; potassium chloride, 0.5 *N*.

1. Reaction of Manganese with Acids

Procedure. Place 3-4 drops of 2 *N* hydrochloric acid into the first test tube, the same amount of 2 *N* nitric acid into the second test tube, and of concentrated sulphuric acid (density 1.84 g/cm³) into the third test tube. Drop a small grain of metal manganese (or 2-3 microspatulas of manganese powder) into each test tube. Observe liberation of gases. What are these gases? Write down the equations for the corresponding reactions, taking into account that manganese(II) salt is produced in all cases. Does manganese dissolve in dilute sulphuric acid? Prove your answer experimentally.

2. Manganese(II) Hydroxide and Its Properties

Procedure. Place 3-4 drops of manganese(II) salt solution into each of two test tubes and add 2-3 drops of 2 *N* alkali solution to both. What is the colour of the precipitated manganese(II) hydroxide? Stir the precipitate in the first test tube using a glass rod and note the development of brown colour due to oxidation of Mn(II) to Mn(IV). Add 2-3 drops of 2 *N* sulphuric acid solution to the second test tube and observe the reaction. What properties are characteristic of manganese(II) hydroxide?

Recording the results. Write down the equations for the reactions by which (a) manganese(II) hydroxide is prepared, and oxidized with atmospheric oxygen to $MnO(OH)_2$; (b) manganese(II) hydroxide reacts with sulphuric acid.

3. Sparingly Soluble Manganese(II) Salts

Procedure. Prepare (a) manganese chromate; (b) manganese carbonate; and (c) manganese sulphide in three test tubes by the reactions between manganese(II) sulphate and potassium chromate, sodium carbonate, and ammonium sulphide, respectively. Take 3-4 drops of each solution for the reaction. Note the colour of the precipitates. Stir the solution with manganese sulphide precipitate using a glass rod. Note the change in the colour of the precipitate. Add 2-4 drops of 2 *N* acid solution to each precipitate and draw your conclusion on solubility of the obtained salts of manganese in an acidic medium.

Recording the results. Write down the equations for the following reactions:

(a) preparing manganese chromate, manganese carbonate and manganese sulphide;

(b) oxidation of manganese sulphide with atmospheric oxygen in the presence of water, taking into consideration that hydroxide of manganese(IV) is produced in this reaction;

(c) dissolution of the chromate, carbonate, and sulphide of manganese(II) in an acid.

4. Reducing Properties of Manganese(II) Compounds

A. Oxidation of manganese(II) salt with bromine

Procedure. Place 2 drops of manganese(II) sulphate solution into a test tube and add 3 drops of 2 *N* sodium hydroxide solution. Add 5-6 drops of bromine water to the obtained precipitate of manganese hydroxide. Observe the change of the colour due to formation of manganese(IV) compound. Write down the reaction equation.

B. Oxidation of manganese(II) salt with sodium bismuthate

Procedure. Place a drop of manganese(II) salt in a test tube and add 5-6 drops of 2 *N* nitric acid solution. Add a small amount (using a microspatula) of sodium bismuthate $NaBiO_3$: observe the colour change of the solution. How does the oxidation state of manganese change in this reaction?

Recording the results. Write down the equation for the reaction in which permanganic acid and bismuth(III) nitrate are formed.

C. Oxidation of manganese(II) salt with ammonium peroxidisulphate

Procedure. Place water in a microflask or a cylindrical test tube to 1/3 its capacity and add 3-4 crystals of ammonium peroxydisulphate $(NH_4)_2S_2O_8$, 2-3 drops of 2 *N* nitric acid solution and of silver nitrate solution (catalyst). Heat the mixture almost to boiling and add a drop of manganese(II) sulphate solution.

Recording the results. Note the colour of the solution and indicate the change of the oxidation state of manganese in the reaction. Write down the equation for the reaction with involvement of water and formation of permanganic acid. Omit nitric acid from the reaction equation.

5. Oxidizing and Reducing Properties of Manganese(IV) Compounds

A. Oxidizing properties of manganese dioxide

Procedure. Place a microspatula of manganese dioxide in a cylindrical test tube and add 2-3 drops of concentrated hydrochloric acid (density 1.19 g/cm^3). Identify the evolving gas by odour and colour. If the reaction is not vigorous, heat carefully the test tube over a low flame of the burner.

Write down the reaction equation.

B. Reducing properties of manganese dioxide

Procedure. Place a small grain of solid sodium hydroxide (*use forceps*!) and of crystalline potassium nitrate in a crucible. Put the crucible on an asbestos-centred gauze or a clay triangle and heat over a burner to melt the mixture (*caution*!). While heating, add a small amount (on a tip of a microspatula) of manganese dioxide. Continue heating until the mass thickens. Note the colour of the melt and save it for the next test.

Write down the equation for oxidation of manganese dioxide with potassium nitrate in an alkaline medium to Na_2MnO_4 (sodium manganate). Potassium nitrate has been converted into what substance?

6. Oxidation-reduction Properties of Manganese(VI) Compounds

A. Disproportionation of manganate in aqueous solution

Procedure. Cool the melt (obtained in the previous test) in the crucible and add water to 1/2 its capacity. Stir the mixture using a glass rod to dissolve the solid. Transfer the solution into three test tubes us-

ing a pipette: 5-6 drops into each test tube. The manganate decomposes slowly in an aqueous solution, the process being accompanied by the reversible disproportionation reaction:

$$Na_2MnO_4 + H_2O \rightleftharpoons NaMnO_4 + MnO_2 + NaOH$$

Place proper coefficients in the equation. In what direction will this equilibrium be shifted if acid is added? Why? Prove your answer experimentally: add 1-3 drops of 2 *N* acetic acid solution to the first test tube and observe development of violet-pink colour in the solution and precipitation of a brown substance. Save two test tubes with the manganate solution for tests *B* and *C*.

Recording the results. Describe the experiment done. Answer the questions. Write down the ionic and molecular equations for disproportionation of the manganate. With which substance does the acetic acid react? Write down the reaction equation. In what medium is manganate stable?

B. Reaction of sodium manganate with chlorine

Procedure. Add 1-3 drops of freshly prepared chlorine water to the second test tube containing the manganate solution. How can the pink colour of the solution be explained? Does Mn^{VI} act as an oxidant or reductant in this reaction? Write down the reaction equation.

C. Reaction of potassium manganate with sodium sulphite

Procedure. Add 1-2 microspatulas of crystalline sodium sulphite to the third test tube: observe decolourization of the solution and precipitation of a brown manganese dioxide. Does Mn^{VI} act as an oxidant or reductant in this process? Sodium sulphite converts into what compound? Write down the reaction equation.

7. Thermal Decomposition of Potassium Permanganate

Procedure. Place 3-4 crystals of potassium permanganate into a cylindrical test tube, fix it in the horizontal position in the stand and heat over a low flame until permanganate completely decomposes into manganese dioxide, potassium manganate, and oxygen. (Prove liberation of oxygen by putting a glowing splint into the test tube.) Cool the test tube and add 5-6 drops of water to the dry residue.

Note the colour of the obtained solution. What substance is dissolved? What substance remains undissolved?

Recording the results. Write down the equation for thermal decomposition of potassium permanganate. Indicate the oxidant and the reductant in this process.

8. Oxidizing Properties of Manganese(VII) Compounds

A. Effect of pH on reduction of permanganate

Depending on whether the medium is acidic or alkaline, manganese(VII) is reduced to its various oxidation states. In an acidic medium MnO_4^- ion converts into Mn^{2+}; in a neutral, weakly alkaline or weakly acidic medium it converts into MnO_2, and in a strongly alkaline medium (in the lack of reductant) into MnO_4^{2-} ion.

Procedure. Place 3-4 drops of potassium permanganate solution into each of three test tubes. Add 2 drops of 2 *N* sulphuric acid solution into the first test tube, the same amount of water into the second, and 3-4 drops of 2 *N* alkali solution into the third test tube. Add a microspatula of crystalline sodium sulphite or potassium sulphite to each test tube. Note the different colour change of the initial permanganate solutions in each test tube. Explain these differences. Write down the equations for the reactions.

B. Oxidation of manganese(II) sulphate with potassium permanganate

Procedure. Place 3-4 drops of a potassium permanganate solution into a test tube and add an equal volume of manganese sulphate solution. Note how the violet colour vanishes and a brown substance precipitates. Dip a blue litmus paper into the solution. What is the medium of the solution? Write down the equation for the reaction if water is involved and potassium sulphate, manganese dioxide, and sulphuric acid are formed.

C. Oxidation of hydrogen peroxide with potassium permanganate

Procedure. Place 3-5 drops of a potassium permanganate solution and 2-3 drops of 2 *N* sulphuric acid solution in a test tube and add 3-4 drops of a 10% solution of hydrogen peroxide. What gas is evolved? How does the oxidation state of manganese change in this reaction? Write down the reaction equation.

D. Oxidation of alcohol with potassium permanganate in an acidic and alkaline medium

Procedure. Place 2-3 drops of potassium permanganate solution into each of two test tubes. Add 2 drops of 2 *N* sulphuric acid solution into one, and of 2 *N* alkali solution into the other test tube. Add 3 drops of ethyl alcohol to the test tube containing acidified solution of potassium permanganate. Heat the solution over a low

flame of a burner. Note the colour change. How does the oxidation state of manganese change in this reaction?

Add 3 drops of ethyl alcohol to the other test tube, containing the alkali potassium permanganate solution. Observe gradual reduction of the permanganate to manganate, and then to manganese dioxide. Note the corresponding change in the solution colour.

Recording the results. Answer the questions. Write down the equations for the following reactions: reduction of potassium permanganate with alcohol in an acidic medium and reduction in an alkaline medium, first to the manganate and then to manganese dioxide, bearing in mind that alcohol is oxidized to the aldehyde in each case.

9. Preparing Sparingly Soluble Perrhenates

Procedure. Place 4-5 drops of ammonium perrhenate solution (NH_4ReO_4) into each of two test tubes and add potassium chloride solution to one, and silver nitrate solution to the other test tube. Observe rapid precipitation of silver perrhenate. Does potassium perrhenate precipitate? Rub the wall of the test tube containing the potassium salt solution with a glass rod (to create crystallization centres). What happens? Write down the equations for the reactions observed. Which salt is less soluble?

10. Rhenium(VII) Sulphide and Its Properties

A. Preparing rhenium(VII) sulphide

Procedure. Place 4-5 drops of ammonium perrhenate solution into a test tube and add 1-2 drops of concentrated hydrochloric acid and 3-4 drops of freshly prepared hydrogen sulphide solution. Observe precipitation of rhenium sulphide Re_2S_7. Save the precipitate for the next test. Write down the equation for the reaction. Is hydrogen sulphide oxidized with ReO_4^- ion? Characterize the reaction of permanganate with hydrogen sulphide. Write down the corresponding reaction equation. Compare the oxidizing properties of Mn^{VII} and Re^{VII}.

B. Preparing thiosalt of rhenium(VII)

Procedure. Using a pipette or filter paper, remove excess liquid from the precipitate of rhenium sulphide prepared in the previous test. Leave only a small portion of the precipitate. Add a few drops of ammonium sulphide solution and stir the mixture using a glass rod. Observe dissolution of rhenium sulphide and formation of the thiosalt of rhenium NH_4ReO_3S. Write down the equation for the reaction with participation of water.

EXPERIMENT 52. SYNTHESIS OF MANGANESE(II) OXALATE

Apparatus and reagents	
Büchner funnel.	Filter paper.
Bunsen flask.	Drying cabinet.
Flask, 150-200-ml, with a stopper.	Balance with a set of weights.
Beakers, 100-ml.	Watch glasses.
Porcelain crucible.	Oxalic acid, crystalline.
	Potassium permanganate, crystalline.
	Distilled water.
	Acetic acid, 2 *N*.

Procedure. Prepare saturated solutions of oxalic acid and potassium permanganate. Act as follows: weigh out 2.34 g of oxalic acid $H_2C_2O_4 \cdot 2H_2O$ and 1.5 g of potassium permanganate. Transfer the salts into two 100-ml conical flasks. Add 10 ml of water into the flask with potassium permanganate and heat the solution to 60 °C. Add 20 ml of water to oxalic acid and heat the flask to boiling. Acidify the hot solution of oxalic acid with 4-5 drops of acetic acid and add slowly, with stirring, the hot solution of potassium permanganate until stable pale pink colour appears. Close the flask with a stopper and allow the solution to stand. When a precipitate coagulates, open the flask and pour off the supernatant liquid carefully. Add distilled water (three times the volume of the precipitate) and shake the flask. Close the flask and allow to stand again. Repeat decantation two times. Transfer the precipitate and the liquid onto a Büchner funnel and wash with water two times. Transfer the filtered crystal hydrate $MnC_2O_4 \cdot 2H_2O$ into a porcelain crucible and dry at a temperature of 150°C in a drying cabinet to remove water of crystallization. Weigh the obtained preparation and handle it over to the laboratory assistant.

Write down the reaction equation:

$$7H_2C_2O_4 + 2KMnO_4 + 2CH_3COOH = 2MnC_2O_4 + 2KCH_3COO + 10CO_2 + 8H_2O$$

Calculate the yield of manganese oxalate in per cent with respect to oxalic acid.

21 Elements of Subgroup VIB

QUESTIONS AND PROBLEMS

1. Write down the electron formulas of chromium and molybdenum atoms. Explain why chromium and molybdenum in the ground state have the electron configuration $(n-1)d^5ns^1$ and not $(n-1)d^4ns^2$.
2. Explain why the atomic radii of molybdenum and tungsten are close while the atomic radius of chromium differs from them.

3. What oxidation states are characteristic of chromium, molybdenum and tungsten? Give examples of the corresponding compounds.
4. Determine the oxidation state of chromium, molybdenum and tungsten in the following compounds:

(a) Cr_2O_3, $BaCrO_4$, $CaCr_2O_7$, $PbMoO_4$;
(b) $Cr_2(SO_4)_3$, $Fe(CrO_2)_2$, $Na_2W_4O_{13}$;
(c) WS_2, WO_3, MoS_2, $PbMoO_4$.

5. Write down the equations for the reactions characterizing the acid-base properties of the following oxides:
(a) Cr_2O_3; (b) CrO_3; (c) MoO_3; (d) WO_3.
6. Indicate which of the following acids is stronger: H_2CrO_4, H_2MoO_4 or H_2WO_4? Explain your answer.
7. Write down the ionic and molecular equations for the reactions between chromium(III) hydroxide and (a) sulphuric acid; (b) potassium hydroxide solution.
8. What are the products of hydrolysis of chromic sulphate and chromic sulphide in dilute aqueous solutions at room temperature? Write down the equations for the corresponding reactions. What substance can weaken the hydrolysis of chromium(III) sulphate solution?
9. Consult the table of standard electrode potentials (Table 11 of Appendix) to decide if potassium dichromate can oxidize in an acidic medium: (a) lead(II) nitrate to PbO_2; (b) iron(II) sulphate to iron(III) sulphate.
10. Solutions of $Cr_2(SO_4)_3$ and $(NH_4)_2S$ react with precipitation of chromium(III) hydroxide. Explain this reaction.
11. How can the following compounds be prepared from chromium(III) oxide: (a) potassium chromate, (b) potassium chromite? Write down the equations for the corresponding reactions.
12. Indicate which ions exist in aqueous solutions of salts of chromium(III) and chromium(VI) (a) at pH < 7; (b) at pH > 7. Give examples of the corresponding compounds and equations for their dissociation.
13. Write down the equations for the reactions by which (a) chromium(III) sulphate can be converted into potassium dichromate; (b) potassium chromate can be converted into chromium(III) chloride; (c) potassium dichromate can be converted into potassium chromate; (d) potassium dichromate can be converted into potassium hexahydroxychromate(III).
14. Complete the following reactions:

(a) $Cr_2O_3 + Na_2CO_3 + KClO_3 =$
(b) $K_2Cr_2O_7 + Zn + H_2SO_4 =$
(c) $K_2Cr_2O_7 + Na_2SO_3 + H_2SO_4 =$
(d) $CrCl_3 + NaOH + H_2O_2 =$
(e) $Na_2Cr_2O_7 + HCl(conc.) =$
(f) $Cr_2(SO_4)_3 + H_2SO_4 + NaBiO_3 =$
(g) $Cr_2(SO_4)_3 + PbO_2 + KOH =$
(h) $K_2Cr_2O_7 + (NH_4)_2S + H_2SO_4 =$
(i) $MoS_2 + HNO_3 =$
(j) $Na_2WO_4 + FeSO_4 + H_2SO_4 =$

15. Write down the coordination formulas and names of the following complex compounds:
(a) $CrCl_3 \cdot 6H_2O$; (b) $3KCN \cdot Cr(CN)_3$; (c) $2KF \cdot WF_6$.
16. Write down the equation for the reaction between potassium dichromate and hydrogen peroxide in an acidic medium with formation of the simplest peroxide of chromium $Cr(O_2)_2O$. Draw its structural formula.
17. Indicate the type of hybridization of molybdenum orbitals and the configuration of the complex ion $[MoF_6]^{3-}$. Is this complex dia- or paramagnetic?

Examples of Multiple-choice Questions

1. What is the electron configuration of the molybdenum atom in the oxidation state of +V?
(1) $...4d^35s^0$; (2) $...4d^55s^1$; (3) $...3d^34s^0$; (4) $...4d^15s^0$; (5) $...4d^25s^0$.
2. What substance precipitates if solutions of $Cr_2(SO_4)_3$ and Na_2S are poured together at room temperature?
(1) Cr_2S_3; (2) $CrOHSO_4$; (3) $Cr(HSO_4)_3$; (4) $Cr(OH)_3$; (5) $Cr_2(OH)_4SO_3$.
3. What is the oxidation state of tungsten in the cation and anion of $(WO_2)_2WO_4$?
(1) +VI in both; (2) +V in both; (3) +VI in the cation and +V in the anion; (4) +V in the cation and +VI in the anion; (5) +III in both.
4. Can a forward reaction occur at STP in the following oxidation-reduction processes (see Table 11 of Appendix):

$$Cr_2O_7^{2-} + 6Fe^{2+} + 14H^+ \rightleftharpoons 2Cr^{3+} + 6Fe^{3+} + 7H_2O$$

(1) forward reaction is possible; (2) reverse reaction is possible; (3) neither reaction is possible.
5. What is the oxidation equivalent of $K_2Cr_2O_7$ in the reaction of its reduction to Cr^{3+}?
(1) $M/3$; (2) $M/4$; (3) $M/2$; (4) $M/8$; (5) $M/6$ (where M is the molecular mass).

EXPERIMENT 53. CHROMIUM

Apparatus and reagents

Crucible. Porcelain crucibles. Asbestos-centred gauze. Iron wire. Water bath. Chromium. Ammonium dichromate. Potassium dichromate. Chromium(III) chloride. Ferrochrome. Potassium nitrate. Potassium carbonate. Potassium pyrosulphate. Diethyl ether. Hydrogen sulphide solution. Litmus, neutral. Solutions: chromium(III) sulphate or ammonium chromic sulphate, 0.5 N; potassium chromate, 0.5 N; potassium dichromate, 0.5 N; sulphuric acid, 2 N; nitric acid, density 1.2 g/cm³; hydrochloric acid, 6 N, density 1.19 g/cm³; sodium hydroxide, 2 N; sodium carbonate, 0.5 N; ammonium sulphide, 0.5 N; lead(II) nitrate, 0.5 N; silver nitrate, 0.1 N; barium chloride, 0.5 N, potassium iodide, 0.5 N; hydrogen peroxide, 3% solution.

1. Reaction of Chromium with Acids

Procedure. Place concentrated hydrochloric acid (6 N) into one test tube and concentrated nitric acid (density 1.2 g/cm³) into another test tube. Drop a grain of chromium or ferrochrome into each test tube. Observe evolution of gas in the first test tube. What gas is it? The solution colours blue (characteristic of Cr^{2+} ions). Does the metal react with the acid in the second test tube? Discard nitric acid, rinse the metal with distilled water and add 6 N hydrochloric acid solution. Does the reaction occur now? What is the effect of nitric acid on chromium?

2. Chromium(III) Oxide and Its Properties

A. Decomposition of ammonium dichromate

Procedure. Place 1/3 test tube of powdered ammonium dichromate on an asbestos-centred gauze and heat. Heat an iron wire in the flame of a burner and dip it into the dichromate. Observe vigorous decomposition of the salt. What is the colour of the obtained chromium(III) oxide?

Recording the results. Write down the equation for the decomposition of the salt bearing in mind that nitrogen and water are also produced in the reaction. Indicate the oxidant and the reductant. What type of reaction is it?

B. Properties of chromium(III) oxide

Procedure. Divide the prepared chromic oxide into two portions and place them in porcelain crucibles. Add equal volume of potassium pyrosulphate $K_2S_2O_7$ into one crucible and the same amount of potassium carbonate into the other. Fuse the mixtures. Cool the melts, transfer them into separate test tubes, and dissolve in a small amount of water. Note the colour of the solutions.

Save the solution in the second test tube (the dissolved melt of chromic oxide with potassium carbonate) for test 4*C*.

Recording the results. Write down the equations for (a) fusion of Cr_2O_3 with $K_2S_2O_7$ which forms yellow K_2CrO_4 and SO_2; (b) fusion of Cr_2O_3 with K_2CO_3 which forms $KCrO_2$. Note the amphoteric properties of chromium(III) oxide.

3. Chromium(III) Hydroxide and Its Properties

Chromium potassium sulphate $KCr(SO_4)_2 \cdot 12H_2O$ can be used instead of chromium sulphate in experiments. When writing down the equations for the reactions, the formula of chromium sulphate $Cr_2(SO_4)_3$ can be put instead of the formula of the alum. Why?

Procedure. Prepare sparingly soluble chromium(III) hydroxide in each of two test tubes by the reaction between chromium(III) salt (3-4 drops) and a 2 *N* solution of alkali (1-2 drops). Try the action of acid and excess alkali on chromium hydroxide. To do so, add, drop after drop, 2 *N* sulphuric acid solution to one test tube, and 2 *N* alkali solution to the other, until the precipitate is dissolved.

Recording the results. Write down the reaction equations for:

(a) preparing chromium(III) hydroxide;

(b) interaction between chromium(III) hydroxide and acid or alkali bearing in mind that the complex anion $[Cr(OH)_6]^{3-}$ is produced in the second case. What is the name of the corresponding po-

tassium salt? As the solution is acidified, the water molecules are gradually substituted for the hydroxide ligands in the hydroxy complex of chromium(III) to give an aqua complex. The coordination number of the complexing agent does not change in this process.

Characterize the chemical (acid-base) character of chromium(III) hydroxide.

Save the solution containing $K_3[Cr(OH)_6]$ for test 5.

4. Hydrolysis of Chromium(III) Salts

A. Hydrolysis of chromium sulphate

Procedure. Try the attitude of litmus to chromium(III) sulphate. To do so, place 3-5 drops of neutral litmus solution into a test tube and add a few crystals of chromium sulphate till the litmus colour changes.

Recording the results. Write down the ionic and molecular equations for the hydrolysis. What substances are produced in this process? Give their names. How can the hydrolysis of this salt be weakened? Or intensified?

B. Simultaneous hydrolysis of chromium sulphate and sodium carbonate

Procedure. Place 2-3 drops of chromium(III) sulphate into a test tube and add, drop after drop, sodium carbonate solution to precipitate $Cr(OH)_3$. Note evolution of gas.

Recording the results. Why has chromium(III) carbonate not been formed? What gas is evolved? Write down the ionic and molecular equations for the reaction. What is the type of hydrolysis of chromium(III) sulphate in this reaction?

C. Hydrolysis of potassium chromite

Procedure. Heat the test tube containing the solution of chromite of the alkali metal (see test 2*B*) in a water bath, or over a burner, to precipitate chromium(III) hydroxide.

Recording the results. Write down the ionic and molecular equations for the hydrolysis of potassium chromite. Indicate the role of heating in this experiment. Which salt, chromium sulphate or potassium chromite, is hydrolized stronger?

5. Reducing Properties of Chromium(III) Salts

Procedure. Add 1-2 drops of alkali and 3-5 drops of a 3% solution of hydrogen peroxide to the solution of $K_3[Cr(OH)_6]$ prepared in test 3. Heat the mixture in a water bath until the green colour changes to yellow indicating formation of potassium chromate in the solution. Write down the equation for the oxidation of $K_3[Cr(OH)_6]$ to K_2CrO_4.

6. Chromates and Dichromates

A. Conversion of potassium chromate to dichromate

Procedure. Place 3-4 drops of potassium chromate solution into a test tube and add, drop after drop, 2 *N* sulphuric acid solution. Note the colour of the initial and resultant solutions and indicate what ions account for these colours. Write down the equation for the reaction. Explain why the prepared salt is a salt of isopolyacid.

B. Conversion of potassium dichromate to chromate

Procedure. Place 3-4 drops of potassium dichromate solution in a test tube and add, drop after drop, an alkali solution until the colour of the solution changes. Write down the reaction equation.

Consider possible displacement of equilibrium in the following system

$$2CrO_4^{2-} + 2H^+ \rightleftharpoons Cr_2O_7^{2-} + H_2O$$

if (a) acid, or (b) alkali is added to it. Which ion, CrO_4^{2-} or $Cr_2O_7^{2-}$, exists in solutions at pH above and below 7?

7. Preparing Sparingly Soluble Chromates

A. Preparing chromates of barium, lead, and silver

Procedure. Place 2-3 drops of potassium chromate solution into three test tubes and add 2-3 drops of barium chloride solution to the first, of lead nitrate to the second, and of silver nitrate to the third test tube. Note the colour of the precipitates.

Write down the ionic and molecular equations for the reactions.

B. Preparing silver dichromate

Procedure. Place 2 drops of 0.1 *N* silver nitrate and of 2 *N* nitric acid solution into a test tube. Shake the test tube and add a crystal of potassium dichromate. What is the colour of the precipitated silver

dichromate? How does the colour of the crystals change in a few seconds due to spontaneous decomposition of silver dichromate into silver chromate and chromium(VI) oxide?

8. Oxidizing Properties of Chromates

A. Oxidation of hydrogen sulphide

Procedure. Place 4-5 drops of potassium dichromate solution acidified with 2-3 drops of 2 *N* sulphuric acid solution into a test tube and add, drop after drop, freshly prepared hydrogen sulphide solution till the solution colour changes. Note turbidity of the solution.

Recording the results. Write down the equation for the reaction. Indicate the reaction product and explain the turbidity of the solution. Chromium(VI) has reduced to what oxidation state? How can this be proved?

B. Oxidation of potassium iodide

Procedure. Place 4-5 drops of a potassium dichromate solution acidified with sulphuric acid in a test tube and add 3-4 drops of potassium iodide solution. Note the colour change. Using starch, prove liberation of free iodine. For this purpose, add a drop of the obtained solution to a test tube containing 5-6 drops of starch solution. Write down the equation for the reaction.

C. Oxidation of hydrochloric acid

Procedure. Place 2-3 drops of potassium dichromate solution in a test tube and add 10-12 drops of concentrated hydrochloric acid (density 1.19 g/cm^3). Heat the mixture till the orange colour changes to green. Observe liberation of gas. How has the oxidation state of chromium changed? What gas is liberated? Write down the equation for oxidation of hydrochloric acid with potassium dichromate.

9. Preparing Chromium Peroxide and Its Decomposition

Procedure. Place 3-4 drops of a potassium dichromate solution acidified with 2-3 drops of 2 *N* sulphuric acid solution into a test tube and add 2-3 drops of diethyl ether $(C_2H_5)_2O$. Add 2-3 drops of a 3% solution of hydrogen peroxide to the obtained mixture and stir thoroughly using a glass rod. Ether extracts the formed peroxide compound because it is more stable in ether than in water. Note the colour of the ether layer. Put the test tube in the rack and observe the colour change and liberation of gas after a certain period of time.

Recording the results. Describe the experiment done and your observations. Write down the equations for the following reactions:

(a) preparing chromium peroxide CrO_5;

(b) conversion of chromium peroxide into the chromium(III) compound in an acidic medium according to the scheme

$$CrO_5 + H_2SO_4 \rightarrow Cr_2(SO_4)_3 + O_2 + H_2O$$

Draw a structural formula for CrO_5.

EXPERIMENT 54. SYNTHESIS OF CHROMIUM POTASSIUM SULPHATE

Apparatus and reagents

Weighing bottle.
Beaker, 100-ml. Cylinders, 10- and 100-ml. Filter paper.
Büchner funnel. Thermometer, scale to 100°C. Potassium dichromate.
Sulphuric acid, density 1.84 g/cm³.
Ethyl alcohol.

Procedure. The main reaction can be expressed as follows:

$$K_2Cr_2O_7 + C_2H_5OH + H_2SO_4 \rightarrow KCr(SO_4)_2 + CH_3CHO + H_2O$$

(Place appropriate coefficients.) Calculate the volume of a 80% solution of ethyl alcohol (density 0.91 g/cm³) which is necessary to reduce 10 g of potassium dichromate. Weigh out 10 g of potassium dichromate on a chemical balance, dissolve in 35-40 ml of water in 100-ml beaker, and add 9 ml of concentrated sulphuric acid (density 1.84 g/cm³) in small portions with stirring. Cool the beaker in snow or cold water. Add (in two or three portions) the calculated amount of alcohol (plus 2 ml) to the cold solution, stir it with a thermometer and see that the temperature does not rise above 40°C. Allow the violet-green solution to stand for crystallization at room temperature for 24 hours. Filter the precipitated crystals of the alum $KCr(SO_4)_2 \cdot 12H_2O$ on a Büchner funnel, wash with the least possible amount of cold water and dry in filter paper. Weigh the obtained alum and calculate its yield. Why is it low? Save the salt in a closed weighing bottle.

Dissolve a portion of this salt in water and use the known reactions to prove the presence of Cr^{3+} and SO_4^{2-} ions in the solution. Write down the equations for the corresponding reactions.

EXPERIMENT 55. MOLYBDENUM

Apparatus and reagents

Zinc granules.
Ammonium molybdate. Diethyl ether.
Solutions: ammonium molybdate, saturated; nitric acid, density 1.2 and 1.4 g/cm³; hydrochloric acid, 2 *N*, density 1.19 g/cm³; sulphuric acid, 2 *N*, density 1.84 g/cm³; calcium chloride, 0.5 *N*; lead nitrate, 0.5 *N*; tin(II) chlorilde, 0.5 *N*; potassium (or ammonium) thiocyanate, 0.5 *N*; sodium hydrogen phosphate, 0.5 *N*; ammonia solution, 25%; sodium hydroxide, 2 *N* and 4 *N*; ammonium polysulphide; hydrogen peroxide, 3% solution.

1. Molybdic Acid and Its Properties

Procedure. Place 3-4 drops of a saturated ammonium molybdate solution $(NH_4)_2MoO_4$ into each of two test tubes and add carefully, drop after drop, one of the strong acids to both (hydrochloric, density 1.19 g/cm³, sulphuric, density 1.84 g/cm³, or nitric, density 1.2 g/cm³) to precipitate molybdic acid. Allow the precipitates to settle. Using a pipette or filter paper, remove the liquid from both test tubes. Add an alkali solution by drops to one test tube and concentrated sulphuric acid to the other. Do the precipitates dissolve?

Recording the results. Write down the equations for the following reactions:

(a) preparing molybdic acid H_2MoO_4;

(b) interaction between molybdic acid and alkali;

(c) interaction between molybdic acid and sulphuric acid by which molybdenum dioxysulphate MoO_2SO_4 is produced. This salt is formed by what base? What is the chemical character of molybdenum(VI) hydroxide?

2. Sparingly Soluble Salts of Molybdic Acid

Procedure. Place 3-4 drops of a saturated ammonium molybdate solution into each of two test tubes and add equal amount of a calcium salt solution to one, and of a lead salt solution to the other test tube. What is the colour of the precipitated substances?

Write down the ionic and molecular equations for the reactions. Give chemical names of the prepared salts.

3. Preparing Molybdenum(VI) Isopolycompound

Procedure. Place a saturated ammonium molybdate solution into a test tube and heat: observe precipitation of crystals of $(NH_4)_6Mo_7O_{24}\cdot nH_2O$. This is an isopolycompound of molybdenum. It can be regarded as a complex compound with the formula $(NH_4)_6[Mo(MoO_4)_6]\cdot nH_2O$.

4. Preparing Heteropolycompound of Molybdenum(VI)

Procedure. Place 5-6 drops of a saturated solution of ammonium molybdate acidified with 1-2 drops of concentrated nitric acid (density 1.4 g/cm^3) and add a drop of sodium hydrogen phosphate solution.

Heat the mixture slightly until yellow ammonium phosphomolybdate $(NH_4)_3[PMo_{12}O_{40}]\cdot 6H_2O$ precipitates. This is the specific reaction for the molybdate ion. The prepared compound is often expressed by another formula:
$(NH_4)_3PO_4\cdot 12MoO_3\cdot 6H_2O$.

5. Preparing Thiosalt and Sulphide of Molybdenum(VI)

Procedure. Place 3-4 drops of an ammonium molybdate solution in a test tube and add, drop after drop, excess solution of ammonium polysulphide until the solution turns red, the colour specific for ammonium thiomolybdate $(NH_4)_2MoS_4$. Ammonium polysulphide $(NH_4)_2S_n$, containing also ammonium sulphide, is commonly used to prevent reduction of molybdenum(VI) with sulphur to its lower oxidation state. Add 2 *N* hydrochloric acid solution to the obtained thiomolybdate by drops to precipitate black molybdenum sulphide MoS_3.

Recording the results. Write down the reaction equations for:

(a) preparing ammonium thiomolybdate $(NH_4)_2MoS_4$ by the interaction of ammonium molybdate with ammonium sulphide;

(b) preparing molybdenum sulphide MoS_3 by the interaction of ammonium thiomolybdate with hydrochloric acid.

Write down the formula of thiomolybdic acid and characterize its stability.

6. Reduction of Ammonium Molybdate(VI)

Procedure. Place 3-4 drops of ammonium molybdate solution acidified with 2-3 drops of hydrochloric acid (density 1.19 g/cm^3) into each of two test tubes and add 1-2 small grains of zinc to one, and a few drops of tin(II) chloride solution to the other test tube until the colour of the formed colloidal solution changes. Compare the reactions in the test tubes.

Recording the results. Write down the equations for the reduction of ammonium molybdate. Take into consideration that the brown colour of the solution obtained during reaction with zinc is characteristic of molybdenum(III) compounds. Tin(II) chloride reduces molybdenum(VI) to the so-called molybdenum blue, a mixture of compounds with the composition from $Mo_2O_5\cdot nH_2O$ to MoO_3, i.e.

compounds in which the oxidation state of molybdenum is (+V) and (+VI). The compound is of the $Mo_4O_{11} \cdot H_2O$ type. It can be described by the formula $2MoO_3 \cdot Mo_2O_5 \cdot nH_2O$. When writing the reaction equation, assume that the product of reduction is Mo_2O_5.

7. Preparing Complex Compound of Molybdenum(V)

Procedure. Place 3 drops of an ammonium molybdate solution into a test tube and add a drop of hydrochloric acid (density 1.19 g/cm³), 3 drops of potassium thiocyanate solution and 2 drops of tin(II) chloride solution. Observe the appearance of red colour due to formation of a complex compound $K_2[MoO(SCN)_5]$. What is the oxidation state of molybdenum in this compound?

Add 2-3 drops of ether to the same test tube, stir using a glass rod, and allow the mixture to stand: observe formation of a coloured ether layer. Ether extracts the complex compound.

Recording the results. Write down the equation for the reaction by which the complex compound of molybdenum is formed, bearing in mind that the reaction occurs in an acidic medium. Indicate the role of tin(II) chloride in this reaction. This reaction is used for detection of molybdenum.

8. Preparing Ammonium Permolybdates

Procedure. Place a crystal of ammonium molybdate into a test tube, add 2-3 drops of 25% ammonium hydroxide solution and 2-3 drops of 3% hydrogen peroxide. Note the colour change due to formation of ammonium permolybdate $(NH_4)_2MoO_x$ (x varies from 5 to 8, depending on the temperature and concentration of hydrogen peroxide).

Write down the reaction equations by which (a) $(NH_4)_2MoO_5$; (b) $(NH_4)_2MoO_6$; (c) $(NH_4)_2MoO_8$ are prepared. Draw the structural formula of the permolybdic acid H_2MoO_6.

EXPERIMENT 56. TUNGSTEN

Apparatus and reagents

Crucible. Clay triangle. Water bath. Ammonium tungstate. Boric acid. Tungsten steel. Zinc granules. Litmus paper, red. Solutions: sodium tungstate, saturated; nitric acid, density 1.4 g/cm³; hydrochloric acid, 2 *N*, density 1.19 g/cm³; sulphuric acid, 2 *N*, density 1.84 g/cm³; sodium hydroxide, 40% solution; calcium chloride, 0.5 *N*; manganese sulphate, 0.5 *N*; lead nitrate, 0.5 *N*; ammonium thiocyanate or potassium thiocyanate, 0.5 *N*; tin(II) chloride, 0.5 *N*; hydrogen peroxide, 30% solution; potassium iodide, 0.1 *N*.

1. Preparing Tungstic Acid

Procedure. Place 3-4 drops of a saturated sodium tungstate(VI) solution into each of two test tubes and add a few drops of a concentrated strong acid (sulphuric, density 1.84 g/cm^3 or hydrochloric, density 1.19 g/cm^3). Note the colour of the precipitate. Remove the liquid above the precipitate in one test tube using a filter paper, and add a few drops of 4 *N* alkali solution. Carefully boil the contents of the second test tube. Observe the colour change. Does the precipitate dissolve on boiling?

Recording the results. The white substance that first precipitates has the composition $H_2WO_4 \cdot H_2O$. The yellow substance obtained after boiling has the composition H_2WO_4. Write down the reaction equation for tungstic acid H_2WO_4 formation and its dissolution in alkali. Note that tungstic and molybdic acids react differently with strong acids.

2. Tungsten Trioxide and Its Properties

Procedure. Place a few crystals of ammonium tungstate in a crucible and put it on a clay triangle over a burner. Heat the crystals until their colour changes. Observe liberation of ammonia (a red litmus paper turns blue).

Write down the equation for the decomposition of ammonium tungstate and indicate the colour of tungsten trioxide. Divide the obtained WO_3 into two portions and place each portion in a separate test tube. Add 3-5 drops of concentrated alkali solution to one, and 3-5 drops of concentrated hydrochloric acid (density 1.19 g/cm^3) to the other test tube. Heat them slightly.

Recording the results. Note the action of acid and alkali on tungsten trioxide. Write down the equations for the reactions. Describe the properties of WO_3.

3. Preparing Sparingly Soluble Tungstates

Procedure. Place 3-4 drops of a saturated sodium tungstate solution into each of three test tubes and add 3-4 drops of a calcium salt solution to the first, of a manganese(II) salt solution to the second, and of lead(II) salt solution to the third test tube.

Recording the results. Note the colour of the precipitates and write down the equations for the reactions.

4. Preparing Heteropoly Compound of Tungsten(VI)

Procedure. Heat a saturated ammonium tungstate solution and add a few crystals of boric acid H_3BO_3 so that some crystals remain undissolved after stirring the solution thoroughly. Transfer a few

drops of the obtained solution into another test tube and check if WO_4^{2-} ions are present by adding a few drops of a manganese(II) or lead(II) salt solution (see test 3). The absence of precipitate indicates formation of a soluble complex salt of a heteropoly acid with 12 tungsten atoms $K_9[BW_{12}O_{42}]$.

Determine the oxidation state of tungsten in the formed complex ion.

5. Reduction of Sodium Tungstate

Procedure. Place 3-4 drops of a saturated sodium tungstate(VI) solution in a test tube and add a few drops of hydrochloric acid (density 1.19 g/cm^3) and a grain of zinc. Heat the test tube and observe first blue colour of 'tungsten blue' and later precipitation of a brown substance WO_2.

Recording the results. The so-called tungsten blue is similar to molybdenum blue and consists of a mixture of compounds in which the oxidation state of tungsten is +V and +VI, (e.g. $WO_2)_2WO_4$. What is the oxidation state of tungsten in the cation and anion of the given compound? Write down the equation for the reaction of sodium tungstate with zinc in hydrochloric acid in which WO_2 is formed.

6. Preparing Tungsten(V) Complex

Procedure. Place a few crystals of ammonium tungstate into a test tube and add 6-8 drops of ammonium thiocyanate solution. Mix thoroughly using a glass rod and add 1-2 drops of hydrochloric acid (density 1.19 g/cm^3) and 2-3 drops of $SnCl_2$ solution.

Recording the results. The obtained yellow-green substance is a complex compound with the formula $(NH_4)_2[WO(SCN)_5]$. What is the oxidation state of tungsten in this compound? Write down the reaction for the formation of this complex compound. Indicate the role of tin(II) chloride in this reaction. It should be noted that only complex compounds of tungsten(V) are stable.

7. Comparing Oxidizing Properties of Tungsten(VI) and Chromium(VI) Compounds

Procedure. Place a few drops of a saturated solution of sodium tungstate(VI) acidified with sulphuric acid into a test tube and add 4-5 drops of potassium iodide. Is iodine liberated in this reaction? Compare the reaction with that described in Experiment 53, test 8*B* (reaction between chromate(VI) solution and potassium iodide).

Compare the oxidizing properties of chromium and tungsten compounds in their higher oxidation states.

8. Sodium Pertungstate

Procedure. Heat 3-4 drops of 30% hydrogen peroxide solution in a test tube and add 5-7 drops of a saturated sodium tungstate solution. Note the yellow colour of sodium pertungstate Na_2WO_x (where x varies from 5 to 8).

Write down the reaction equations for preparing (a) Na_2WO_5; (b) Na_2WO_8. Draw their structural formulas.

9. Detecting Tungsten in Steel

Procedure. Place a small amount (about 0.02-0.03 g) of finely crushed steel in a porcelain crucible and dissolve it in 12-15 drops of 2 *N* sulphuric acid solution with heating. The evolving hydrogen is the product of what reaction? After the hydrogen stops evolving, add, drop by drop, concentrated nitric acid (density 1.4 g/cm^3) and continue heating until foaming stops. The carbides and carbon contained in the black precipitate are oxidized. If tungsten is present, a yellow tungstic acid H_2WO_4 will precipitate in a few minutes.

Another specific reaction for tungsten is formation of tungsten blue. To that end cool the crucible and add carefully 15-20 drops of distilled water, pour off the liquid from the precipitate, and transfer the remaining suspension into a test tube. Remove all liquid using filter paper, wash the precipitate with dilute hydrochloric acid, and remove the liquid phase again. Add a few drops of concentrated hydrochloric acid and 3-5 drops of $SnCl_2$ solution. If tungsten(VI) is present, the blue colour (tungsten blue) appears after a certain period of time.

22 Elements of Subgroup VB

QUESTIONS AND PROBLEMS

1. Write down the formulas for vanadium oxides and indicate how their chemical properties change in the transition from the lower to the higher oxidation state.
2. Which of the oxides has a stronger acid properties: (a) V_2O_5 or Nb_2O_5; (b) V_2O_5 or As_2O_5?
3. Determine the oxidation state of vanadium in the following ions: $V_4O_9^{2-}$, VO^{2+}, $V_3O_9^{3-}$, $V_{10}O_{28}^{6-}$, $V_2O_4^{+}$, VO_2^{+}. Write down the formulas of compounds containing said ions (one example for each ion).
4. Write down the equations for the reaction in which (a) sodium metavanadate $NaVO_3$ converts into the decavanadate $Na_6V_{10}O_{28}$;
(b) sodium metavanadate $NaVO_3$ converts into a salt containing VO_2^{+} ion.
5. Write down the equations for the following reactions:
(a) preparing sodium thiovanadate $NaVS_3$ from vanadium(V) sulphide;

(b) preparing $NaVS_3$ from sodium metavanadate;
(c) interaction of $NaVS_3$ with hydrochloric acid.
6. Draw a structural formula for $VO(ClO_4)_2$ and indicate the oxidation state of vanadium in this compound.
7. Complete the following equations and place proper coefficients for the following oxidation-reduction reactions:
(a) $Na_6V_{10}O_{28} + Al + HCl = VCl_2 + \ldots$
(b) $VOSO_4 + K_2Cr_2O_7 + H_2O = H_3VO_4 + \ldots$
8. Write down the standard electrode potentials in acidic medium (see Table 11 of Appendix) for the following systems:
(a) $VO_2^+ \rightarrow VO^{2+}$; (b) $VO_2^+ \rightarrow V^{3+}$; (c) $VO_2^+ \rightarrow V^{2+}$. Which of the following substances: H_2S, KI, Na_2SO_3, $FeSO_4$, or Zn should be used to reduce in an acidic medium: (a) VO_2^+ to VO^{2+}; (b) VO_2^+ to V^{3+}; (c) VO_2^+ to V^{2+}? Write down the equations for the corresponding reactions.
9. Write down the equation for the reaction of metavanadic acid with hydrogen peroxide with the formation of the simplest pervanadic acid, and draw the structural formula of this acid.
10. Niobium dissolves in a mixture of nitric and hydrofluoric acid to form a complex dibasic acid of niobium(V) in which the fluoride ions F^- are the ligand and the coordination number of niobium(V) is 7. Write down the equation for the reaction and place proper coefficients assuming that nitric acid is reduced to NO in this reaction.

Examples of Multiple-choice Questions

1. The ending of the electron formula $\ldots 5d^3 6s^2$ belongs to which element?
(1) Nb; (2) Ta; (3) V; (4) Sb; (5) As.
2. What oxidation state is more stable for vanadium?
(1) (I); (2) (II); (3) (III); (4) (IV); (5) (V).
3. Write down the equation for aluminothermic preparation of vanadium from V_2O_5. What is the sum of the coefficients in the left part of the equation?
(1) 10; (2) 11; (3) 13; (4) 24; (5) 12.
4. Which ion of vanadium(V) is mainly formed in a strongly acidic solution?
(1) VO_3^-; (2) $V_2O_7^{2-}$; (3) $V_{10}O_{28}^{6+}$; (4) VO^{3-}; (5) VO_2^+.
5. What reductants can convert VO_2^+ into V^{2+} in an acidic medium if, for the system $VO_2^+ + 4H^+ + 3\bar{e} = V^{2+} + 2H_2O$, $\varphi^\circ = 0.36$ V?
(1) $NaBrO_3$; (2) $FeSO_4$; (3) Zn; (4) Al; (5) KI.

EXPERIMENT 57. VANADIUM. NIOBIUM

Apparatus and reagents

Water bath.
Porcelain dish. Ammonium metavanadate.
Tin granules. Oxalic acid.
Vanadium(V) oxide.
Sodium sulphite. Zinc.
Ferrovanadium. Iron powder.
Solutions: litmus, neutral; sodium hydroxide, 2*N*, 4 *N*; potassium hydroxide, 40% solution; sulphuric acid, 2 *N*, 1:3, density 1.84 g/cm³; hydrochloric acid, 2 *N*, density 1.19 g/cm³; nitric acid, 1:1; sodium (or ammonium) metavanadate, saturated; barium chloride, 0.5 *N*; copper(II) sulphate, 0.5 *N*; silver nitrate, 0.1 *N*; lead nitrate, 0.5 *N*; potassium permanganate, 0.5 *N*; hydrogen peroxide, 3% solution; ammonium (or sodium) sulphide, 0.5 *N*; potassium niobate, saturated.

1. Vanadium(V) Oxide

Procedure. (*Use the hood!*). Place two microspatulas of dry ammonium metavanadate NH_4VO_3 in a porcelain dish and heat carefully with stirring using a glass rod. Observe the conversion of white ammonium vanadate into brick-red vanadium(V) oxide.

Divide the prepared oxide into two portions and place each in separate test tubes. Add 4-5 drops of 2 *N* sodium (or potassium) hydroxide solution into the first test tube, and of concentrated sulphuric acid into the other. Heat the second test tube in a water bath: observe dissolution of vanadium(V) oxide in an acidic and alkaline medium, and note the colour of the prepared solutions.

Recording the results. Write down the equations for the following reactions: (a) decomposition of ammonium metavanadate; (b) interaction of vanadium(V) oxide with alkali and sulphuric acid, bearing in mind that $NaVO_3$ is produced in the first reaction and $(VO_2)_2SO_4$ in the second reaction. Draw your conclusion on the chemical character of vanadium(V) oxide.

2. Vanadic Acids and Their Salts

A. Preparing metavanadic acid

Procedure. Place a microspatula of powdered vanadium(V) oxide in a cylindrical test tube and add 5-7 drops of distilled water. Heat the mixture until the solution turns pale yellow.

Using a pipette, transfer a few drops of the obtained solution into a test tube containing neutral litmus. Observe the colour change.

Write down the equation for the reaction by which metavanadic acid is prepared.

B. Conversion of metavanadate ion into decavanadate ion

Procedure. Place 3-4 drops of a saturated sodium metavanadate solution $NaVO_3$ into a test tube and add 1-2 drops of concentrated sulphuric acid (density 1.84 g/cm^3). Note the appearance of yellow colour in the solution.

Recording the results. Metavanadates convert in an acidic medium into polyvanadates which are salts of polyvanadic acids with the general formula $xV_2O_5 \cdot yH_2O$. The most stable of them are decavanadic acid $H_6V_{10}O_{28}$ and its salts, decavanadates.

Write down the ionic and molecular equations for the reaction by which sodium metavanadate is converted into the decavanadate. Express the formula of decavanadic acid in terms of vanadium(V) oxide and water. Why is decavanadic acid a polyacid?

C. Preparing sparingly soluble vanadates

Procedure. Place 3-4 drops of sodium metavanadate solution into each of four test tubes and add 3-4 drops of barium chloride solution into the first test tube, of copper sulphate into the second, of silver nitrate into the third, and of lead nitrate into the fourth test tube. Observe precipitation and note the colour of the precipitates.

Recording the results. Write down the ionic and molecular equations for the corresponding reactions bearing in mind that barium and lead form metavanadates while silver forms the salt of orthovanadic acid H_3VO_4. Depending on pH of a solution, copper can form bluish-green metavanadates, or yellow-green orthovanadates.

3. Preparing Thio Salt and Sulphide of Vanadium(V)

Procedure. Place a few crystals of sodium metavanadate(V) in a test tube and add, drop by drop, ammonium (or sodium) sulphide until red colour appears due to formation of ammonium thiovanadate $(NH_4)_3VS_4$. Add, drop by drop, 2 *N* hydrochloric acid solution to precipitate a brown vanadium sulphide V_2S_5. The evolving hydrogen sulphide can partly reduce vanadium(V) to vanadium(IV) and the solution will become blue.

Recording the results. Write down the equations for the following reactions:

(a) preparing ammonium thio-orthovanadate, bearing in mind that water is involved in the reaction;

(b) interaction of ammonium thiovanadate with hydrochloric acid to form thio-orthovanadic acid;

(c) decomposition of the thio acid.

4. Compounds of Vanadium(IV)

A. Vanadium(IV) oxide and its properties

Procedure. Mix a few crystals of oxalic acid $H_2C_2O_4$ and the same amount of powdered vanadium(V) oxide in a dry cylindrical test tube. Fix the test tube in the stand and heat the mixture. Observe the formation of dark blue vanadium(IV) oxide. Transfer a portion of the obtained dioxide into each of two test tubes and add 4-5 drops of 2 *N* alkali solution into one and the same volume of 2 *N* sulphuric acid solution into the other test tube. Heat carefully both to dissolve the precipitate. Note the colour of the obtained solutions.

Recording the results. Write down the equations for the following reactions:

(a) reduction of vanadium(V) oxide with oxalic acid (carbon dioxide is evolved during the reaction);

(b) interaction of vanadium dioxide with sodium hydroxide (sodium tetravanadate(IV) $Na_2V_4O_9$ is the product of the reaction);
(c) interaction of vanadium dioxide with sulphuric acid (vanadium(IV) oxysulphate $VOSO_4$ is the reaction product).
Draw your conclusion on the character of vanadium(IV) oxide.

B. Reduction of vanadate(V) to vanadate(IV)

Procedure. Place 5 drops of a saturated metavanadate(V) solution into a test tube and add 3-4 drops of concentrated HCl. Note the colour change. Add a few crystals of sodium sulphite and shake the test tube until the solution turns blue (the colour is specific for VO^{2+} ion). Save the solution for the next test.
Write down the equations for the:
(a) conversion of sodium metavanadate into vanadium(V) dioxychloride VO_2Cl in a strongly acidic medium;
(b) reduction of VO_2Cl to $VOCl_2$.
Why cannot vanadium(IV) chloride be prepared in an aqueous solution?

C. Properties of vanadium(IV) hydroxide

Procedure. Add carefully, drop by drop, 2 *N* alkali solution to the solution of vanadium(IV) oxychloride prepared in the previous test. Observe the formation of a brown suspension of vanadium(IV) hydroxide. Divide the suspension into two test tubes and test the action of acid and excess alkali on the obtained hydroxide.
Draw your conclusion on the character of vanadium(IV) hydroxide. Write down the equations for the following reactions: (a) preparing vanadium(IV) hydroxide; (b) its dissolution in acid; (c) its dissolution in alkali with formation of $Na_2V_4O_9$.

5. Vanadium(III) Compounds

A. Reduction of vanadium(V) to vanadium(III)

Procedure. Place 5 drops of sodium metavanadate(V) into a test tube and add 5 drops of concentrated hydrochloric acid (density 1.19 g/cm^3). Add a grain of tin to the solution and heat over a low flame of the burner. Observe the appearance of blue colour (VO^{2+}) and the change of the colour to green, which is characteristic of V^{3+}. Save the solution for the next test.
Write down the equation for the reduction of vanadium(V) to VCl_3.

B. Properties of vanadium(III) hydroxide

Procedure. Place 2-3 drops of the green solution of VCl_3 prepared in the previous test into each of two test tubes and add a few drops of 4 *N* alkali solution to each test tube to precipitate dark vanadium(III) hydroxide. Test the action of acid and alkali on the obtained hydroxide. Why does the presence of $Sn(OH)_2$ not interfere with the study of properties of $V(OH)_3$?

Recording the results. Draw your conclusion on the properties of vanadium(III) hydroxide. Write down the equations for the reactions by which vanadium(III) hydroxide is prepared and dissolved in acid.

6. Consecutive Reduction of Vanadium(V) Compounds to Vanadium(II) Compounds

Procedure. Place 12-15 drops of a saturated sodium metavanadate solution into a test tube and add 8-10 drops of concentrated hydrochloric acid and 2-3 grains of zinc.

Observe consecutive change in the colour of the solution. As a new shade of colour appears, transfer three drops of the solution into separate test tubes.

Recording the results. Note and explain the consecutive colour change from yellow to green, then to blue, again green, and finally lilac (violet). Write down the equations for the reactions of consecutive reduction of vanadium compounds and reduction of sodium metavanadate with the formation of vanadium(II) chloride. Save the solution for the next test.

7. Vanadium(II) Hydroxide

Transfer small portions of the lilac solution prepared in the previous test into two test tubes and add, drop by drop, 4 *N* alkali solution to both to precipitate vanadium(II) hydroxide. Test the action of acid and excess alkali on $V(OH)_2$.

Add, by drops, a potassium permanganate solution to the obtained solution of vanadium(II) hydroxide. Observe the colour change of the permanganate.

Recording the results. Draw a conclusion on the acid-base properties of vanadium(II) hydroxide. Bear in mind that the precipitate dissolves partly in excess alkali due to dissolution of zinc hydroxide (Zn^{2+} ions are formed during oxidation of metallic zinc in test 6). What properties of vanadium(II) are demonstrated in the oxidation-reduction reaction? Write down the equations for all reactions observed.

8. Preparing a Mixture of Pervanadic Acids

Procedure. Place 4-5 drops of a saturated sodium metavanadate(V) solution into a test tube and add a few drops of 3% hydrogen peroxide solution and a few drops of 2 *N* sulphuric acid solution.

Note the red colour of the resultant solution which is due to the formation of a mixture of pervanadic acids and note the liberation of oxygen which indicates their instability.

Write down the equation for the reaction by which the simplest pervanadic acid HVO_4 is formed. Draw a structural formula of this acid.

9. Niobium(V) Hydroxide

Procedure. Place 8-10 drops of potassium niobate solution $KNbO_3$ into each of two test tubes and add an equal volume of 2 *N* sulphuric acid solution to both. Observe precipitation of a white jelly-like substance with a variable composition $Nb_2O_5 \cdot xH_2O$.

Examine the properties of the precipitated hydroxide. To do so, add 5-6 drops of 40% KOH solution into one test tube and a few drops of sulphuric acid (density 1.84 g/cm^3) into the other to dissolve the precipitates.

Write down the equations for the reactions by which metaniobic acid is formed and dissolved in alkali and acid, assuming that $(NbO_2)_2SO_4$ is formed in an acidic medium.

Save the solution of niobium dioxysulphate for tests 10 and 11.

10. Hydrolysis of Niobium(V) Salts

Procedure. Place 20-25 drops of distilled water in a test tube and heat to boiling. Add 3-4 drops of niobium dioxysulphate prepared in the previous test. Observe precipitation of a jelly-like substance.

Write down the equation for the hydrolysis of niobium dioxysulphate assuming that niobium dioxyhydroxide precipitates.

11. Reduction of Niobium(V) Compounds to Niobium(III) Compounds

Procedure. Place 10-15 drops of niobium dioxysulphate in a test tube and add 5-6 drops of hydrochloric acid (density 1.19 g/cm^3) and a microspatula of powdered iron. Heat the test tube carefully until a stable blue colour appears (the colour characteristic of niobium(III)).

Write down the equation for the reduction of niobium(V) compound bearing in mind that iron is oxidized to iron(II).

12. (Control Test)

Detecting vanadium in ferrovanadium. Place 2-3 microspatulas of fine powder of ferrovanadium in a porcelain dish (d = 3 cm). Add 5 drops of a nitric acid solution (1:1) and stir using a glass rod to dissolve ferrovanadium. Add 5 drops of sulphuric acid (1:3) and heat until white fumes of SO_3 evolve.

Allow the prepared solution to cool and transfer 5-6 drops into a test tube containing a few drops of distilled water. Add hydrogen peroxide as instructed in test 8. Does the red colour, specific for peroxy acids of vanadium(V), appear?

23 Elements of Subgroup IVB

QUESTIONS AND PROBLEMS

1. Indicate the differences in the structure of the atoms of titanium and germanium. How do these differences influence the character of their oxides and hydroxides?
2. What properties (oxidizing or reducing) do titanium(III) and titanium(IV) compounds exhibit in chemical reactions?
3. Which of the two hydroxides has a stronger basic properties: (a) $Ti(OH)_4$ or $Zr(OH)_4$; (b) $Ti(OH)_4$ or $Ti(OH)_3$? Explain your answer.
4. Calcining of metallic titanium in air gives a white powder soluble in concentrated sulphuric acid and fusible with alkalies. What is this white powder? Write down the equaions for the following reactions:
(1) calcining of titanium in air;
(2) fusing titanium dioxide with alkali;
(3) dissolution of titanium dioxide in sulphuric acid.
5. Write down the equation for hydrolysis of zirconium and titanium tetrachlorides. In which case the hydrolysis degree is higher? Explain your answer.
6. Draw structural formulas for titanium(IV) oxysulphate and zirconium(IV) oxynitrate. Write down the reaction of their formation during the hydrolysis of the corresponding neutral salts.
7. As an acidified colourless solution of a titanium(IV) salt reacts with zinc, the solution turns violet. Explain this reaction and write down the equation.
8. When hydrogen peroxide solution is added to a weakly acidic solution of zirconium tetrachloride, white H_2ZrO_5 precipitates. Write down the reaction equation and the structural formula for the obtained compound.
9. As a small quantity of ammonium oxalate is added to zirconium tetrachloride, a white substance precipitates which is soluble in excess ammonium oxalate. Write down the equations for the reactions.

Example of Multiple-choice Questions

1. Which ending of the electron formula corresponds to the hafnium atom? (1) $...5d^25p^2$; (2) $...4d^35s^2$; (3) $...6s^26p^2$; (4) $..5d^26s^2$; (5) $...5d^36s^1$.
2. What are the properties of titanium dioxide TiO_2?

(1) acid; (2) basic; (3) amphoteric; (4) nonsalt-forming.
3. What substance forms in hydrolysis of titanium tetrachloride when its dilute solution is boiled?
(1) $Ti(OH)_3Cl$; (2) $Ti(OH)Cl_3$; (3) $Ti(OH)_4$; (4) $TiOCl_2$; (5) $TiO(OH)_2$.
4. What is the sum of coefficients in the equation

$$Ti + HCl \rightarrow TiCl_3 + H_2$$

(1) 11; (2) 12; (3) 13; (4) 14; (5) 15.
5. Which of the following compounds is pertitanic acid?
(1) $Ti(OH)_4$; (2) H_4TiO_4; (3) H_4TiO_5; (4) $TiOSO_4$; (5) H_2TiO_3.

EXPERIMENT 58. TITANIUM. ZIRCONIUM

Apparatus and reagents

Microflask.
Titanium, powder or chips. Zinc granules. Litmus paper, blue and red. Solutions: hydrochloric acid, 4 *N*, density 1.19 g/cm³; sulphuric acid, 4*N*, density 1.84 g/cm³; sodium hydroxide, 4 *N*; titanium oxysulphate, 0.5 *N*; zirconium oxychloride, 0.5 *N*; copper(II) chloride, 0.1 *N*; iron(III) chloride, 0.5 *N*; ammonium sulphide, 0.5 *N*; hydrogen peroxide, 3% solution; sodium hydrogen phosphate, 0.5 *N*; ammonium oxalate, 0.5 *N*.

1. Reaction of Titanium with Acids

Place titanium powder or chips into each of two test tubes and add 5-6 drops of 4 *N* hydrochloric acid into the first test tube, and of 4 *N* sulphuric acid into the second test tube. Conduct a similar experiment with concentrated hydrochloric and sulphuric acids (density 1.19 g/cm³ and 1.84 g/cm³, respectively). Carefully heat those test tubes where the reaction proceeds slowly.

In which test tubes has the solution turned violet, the colour specific for the hydrated titanium(III) ions? Identify by odour the gas that evolves in the reaction between titanium and concentrated sulphuric acid. What gases are evolved in the other test tubes?

Recording the results. Write down the equations for the reactions observed. The reaction of titanium with concentrated sulphuric acid gives the salt $Ti(SO_4)_2$. $Ti_2(SO_4)_3$ has formed in solutions that turned violet. Why does dissolution of titanium in dilute and concentrated sulphuric acid give compounds of titanium in different oxidation states?

Nitric acid passivates titanium to form a dense oxide film on its surface. If the film is destroyed, titanium is oxidized to metatitanic acid H_2TiO_3, that precipitates as a jelly-like substance. Write down the equations for the reactions between titanium and dilute and concentrated nitric acid (nitrogen oxide is evolved in the reaction with dilute acid and nitrogen dioxide in the reaction with concentrated nitric acid).

2. Hydrolysis of Titanium(IV) Salts

A. Hydrolysis of titanium sulphate

Procedure. Place 3-4 drops of titanium(IV) oxysulphate $TiOSO_4$ (titanyl sulphate) into a test tube and add 8-10 drops of distilled water. Boil the solution for 2-3 minutes and observe precipitation of a white substance.

Recording the results. Titanium oxysulphate $TiOSO_4$ rather than the neutral salt $Ti_2(SO_4)_2$ is commonly used to study the properties of titanium compounds, because the neutral salt hydrolyzes in aqueous solutions. At which step of $Ti(SO_4)_2$ hydrolysis is $TiOSO_4$ formed? The hydrolysis occurs at room temperature.

Write down the equations for the following reactions:

(a) hydrolysis of the neutral salt in the cold to form titanyl sulphate;

(b) hydrolysis of titanyl sulphate with boiling with precipitation of a sparingly soluble hydroxide $TiO(OH)_2$.

B. Mutual hydrolysis of titanyl sulphate and ammonium sulphide

Procedure. Place 3-4 drops of titanyl sulphate solution into a test tube and add the same volume of ammonium sulphide solution. Observe precipitation of titanium hydroxide. Why does titanium(IV) sulphide not precipitate?

Recording the results. Write down the equation for the reaction between titanyl sulphate and ammonium sulphide in an aqueous solution. The hydrolysis of titanyl sulphate in the presence of ammonium sulphide is complete at room temperature. Why?

3. Titanium(IV) Hydroxide

Procedure. Place 3 drops of titanyl sulphate $TiOSO_4$ into each of three test tubes and add, drop by drop, 4 *N* alkali solution to precipitate titanium(IV) hydroxide. Note the colour of the precipitate.

Add 5-6 drops of 4 *N* sulphuric acid solution to one test tube. Does the precipitate dissolve? Boil the suspension in the second test tube for 3-4 minutes and test again the solubility of the precipitate in 4 *N* sulphuric acid. Add 5-6 drops of 4 *N* alkali solution to the third test tube: the amphoteric hydroxide $TiO(OH)_2$ is practically insoluble in aqueous alkali solutions.

Recording the results. Write down the equations for the reactions by which titanium(IV) hydroxide is prepared and by which the freshly precipitated substance is dissolved in dilute sulphuric acid to form $TiOSO_4$. Why is $Ti(SO_4)_2$ not formed by this reaction?

Insolubility of the precipitate in sulphuric acid after boiling is explained as follows. Titanium hydroxide, whose composition is commonly expressed by the formula $TiO(OH)_2$ has a variable

composition. When just precipitated, it has a greater number of the OH groups, but while the precipitate stands or is boiled, it loses these OH groups and becomes less soluble.

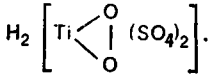
Acidic properties of titanium(IV) hydroxide which acts as an acid H_2TiO_3 (metatitanic acid) are only demonstrated during its fusion with alkalies to form metatitanates. Do acid or basic properties prevail in the amphoteric hydroxide of titanium(IV)?

4. Preparing Pertitanic Acid

Procedure. Place 3-4 drops of titanium sulphate solution and of 4 *N* sulphuric acid solution in a test tube. Add 2-3 drops of 3% hydrogen peroxide solution and observe the appearance of orange colour, specific for pertitanic acids.

Recording the results. Write down the equation for the reaction by which the simplest pertitanic acid H_4TiO_5 is formed from a titanium(IV) salt, water, and hydrogen peroxide. Draw its structural formula by replacing one —OH group in the titanium hydroxide $Ti(OH)_4$ by one —O—OH group.

Note: A mixture of pertitanic acids is formed in this reaction: disulphopertitanic acid



prevails among them.

5. Preparing Titanium(III) Sulphate

Procedure. Place 12-15 drops of titanyl sulphate solution into a test tube and add 5-6 drops of 4 *N* sulphuric acid solution and a grain of zinc. Heat carefully the test tube until its contents colours violet, the colour specific for Ti^{3+} ions. Transfer 2-3 drops of the solution into another test tube and shake for 2-3 minutes. How does the colour of the solution change?

Recording the results. Write down the equations for the following reactions:

(a) reduction of titanyl sulphate to titanium(III) sulphate;

(b) back oxidation of $Ti_2(SO_4)_3$ to the salt of titanium(IV) with atmospheric oxygen with involvement of water.

Save the solution for tests 6, 7 and 8.

6. Preparing Titanium(III) Hydroxide

Procedure. Place 2-3 drops of the titanium(III) salt solution prepared in the previous test into a clean test tube and add 2-3 drops of an alkali solution.

What is the colour of titanium(III) hydroxide precipitate? Compare it with the colour of titanium(IV) hydroxide (see test 3). Remove the liquid phase from the precipitate. Stir the precipitate carefully using a glass rod. How does the colour of the precipitate change?

Recording the results. Write down the equations for the reactions by which $Ti(OH)_3$ is prepared and oxidized to $TiO(OH)_2$ with atmospheric oxygen.

Which oxidation state is more characteristic and stable for titanium?

7. Reducing Properties of Titanium(III) Compounds

A. Reduction of copper(II) chloride

Procedure. Place 2-3 drops of the titanium(III) salt solution (prepared in test 5) into a test tube and add 1-2 drops of copper(II) chloride solution. Compare the colour of the obtained solution with that of the initial solution. What is the white substance that precipitates in this reaction?

Write down the equation for the reaction by which copper(II) is reduced with titanium(III) to copper(I).

B. Reduction of iron(III) chloride

Procedure. Place 2-3 drops of the titanium(III) salt solution prepared in test 5 into a test tube and add 2-3 drops of $FeCl_3$ solution and observe vanishing of the violet colour.

Write down the equation for the reaction by which iron(III) chloride is reduced with titanium(III) sulphate to iron(II) chloride.

C. Reduction of potassium permanganate

Procedure. Place 2-3 drops of the $Ti_2(SO_4)_3$ solution (prepared in test 5) into a test tube and add, drop by drop, a potassium permanganate solution. How does the colour of potassium permanganate change? To what oxidation state is manganese(VII) reduced in an acidic medium?

Write down the equation for the reaction. How does this oxidation-reduction reaction agree with the corresponding standard electrode potentials? See Table 11 of Appendix.

8. Change of Properties of Titanium Hydroxides with Oxidation State of Titanium

Procedure. Place 3-4 drops of titanium(IV) and of titanium(III) sulphate solutions into two separate test tubes and add 8-10 drops of distilled water to each. Boil the solutions. In which case has titanium hydroxide precipitated due to hydrolysis of the salt? Which hydroxide, $Ti(OH)_3$ or $TiO(OH)_2$, has stronger basic properties?

9. Zirconium(IV) Hydroxide

Procedure. Prepare a sparingly soluble zirconium(IV) hydroxide $ZrO(OH)_2$ in each of three test tubes by adding 1-2 drops of 4 *N* alkali solution to 2-3 drops of zirconium oxychloride (zirconyl chloride) $ZrOCl_2$. Boil the contents in one test tube (*Caution*) for 2-3 minutes, cool, and add 4-5 drops of hydrochloric acid (density 1.19 g/cm^3). Add an equal volume of hydrochloric acid to a freshly prepared (not boiled) zirconium hydroxide precipitate in the second test tube. In which test tube has the precipitate dissolved? Add 4-5 drops of 4 *N* alkali solution to the third test tube. Has the precipitate dissolved?

Recording the results. Write down the reaction equations for
(a) preparing zirconium hydroxide $ZrO(OH)_2$*;
(b) interaction of the hydroxide with hydrochloric acid.

Why has this hydroxide not dissolved in hydrochloric acid after boiling?

Zirconium(IV) hydroxide is amphoteric, but zirconates can only be prepared by fusion of zirconium dioxide with alkalies.

10. Hydrolysis of Zirconium(IV) Salts

A. Hydrolysis of zirconium(IV) chloride

Procedure. Place 2-3 crystals of zirconium tetrachloride in a test tube. Why does the substance fume in air? Add 6-8 drops of distilled water, mix, and apply a drop on red and blue litmus paper. Does the aqueous solution of $ZrCl_4$ react acid or basic? Explain. Add distilled water to the prepared solution to 1/2 of the test tube capacity, stir and boil. Observe precipitation of zirconium(IV) hydroxide.

Recording the results. Write down the equations for the following reactions:

* The precipitate has actually a variable composition of $ZrO_2 \cdot nH_2O$.

(a) hydrolysis of zirconium chloride $ZrCl_4$ without heating to form zirconyl chloride $ZrOCl_2$;

(b) hydrolysis of the prepared salt during boiling the solution with precipitation of $ZrO(OH)_2$.

B. Hydrolysis of zirconyl chloride in the presence of ammonium sulphide

Procedure. Place 3-5 drops of a zirconium(IV) oxychloride solution into a test tube and add an equal volume of ammonium sulphide. Observe precipitation of white zirconium hydroxide. Write down the equation for simultaneous hydrolysis of zirconyl chloride and ammonium sulphide.

11. Preparing Sparingly Soluble Zirconates

Procedure. Place 3-5 drops of zirconyl chloride in each of three test tubes and add equal volumes of sodium hydrogen phosphate Na_2HPO_4 to the first, of potassium ferrocyanide $K_4[Fe(CN)_6]$ to the second, and of ammonium oxalate $(NH_4)_2C_2O_4$ to the third test tube. Observe precipitation of white zirconium hydrogen phosphate, zirconium ferrocyanide, and zirconyl oxalate, respectively.

Write down the equations for the reactions by which the precipitates are formed, bearing in mind that the reaction of the zirconium salt with ammonium oxalate occurs with involvement of water.

Save the zirconyl oxalate for the next test.

12. Preparing a Complex Compound of Zirconium

Procedure. Add 5-8 drops of ammonium oxalate to the test tube containing zirconyl oxalate prepared in the previous test and observe dissolution of the precipitate and formation of a complex compound with the formula $(NH_4)_2[ZrO(C_2O_4)_2]$. Write down the reaction equation.

24 Elements of Subgroup IIIB

QUESTIONS AND PROBLEMS

1. How do the atomic radii of the lanthanides change with their increasing atomic numbers? What effects do these changes have on some properties of the *d* elements of the 4th period compared with the properties of *d* elements of the 5th and 6th periods found in similar subgroups?

2. What oxidation states are characteristic of the lanthanides and actinides in their compounds? How can their variation be explained?
3. Write down the electron formulas for all lanthanides. Can any periodicity be traced in their electron structures? Which lanthanides are paramagnetic in their ground states?
4. Write down the equation for the reaction between cerium(III) sulphate and ammonium persulphate in an acidic medium.
5. Write down the equation for the oxidation of cerium(III) nitrate with potassium permanganate in the presence of soda.
6. What is the difference in the properties of cerium compounds and other rare earth elements?

EXPERIMENT 59. LANTHANUM. CERIUM

Apparatus and reagents

Lanthanum oxide.
Solutions: nitric acid, 2 *N*; oxalic acid, 1 *N*; sodium hydroxide, 2 *N*; lanthanum nitrate, 2 *N*; cerium (III) nitrate, 2 *N*; cerium(IV) nitrate, 2 *N*; sodium phosphate, 1 *N*; sodium fluoride, 1 *N*; hydrogen peroxide, 3%, 30% solutions;
potassium iodide, 0.2 *N*.

1. Preparing Lanthanum Hydroxide

A. Reaction of lanthanum oxide with water

Procedure. Place 2 microspatulas of lanthanum oxide in a test tube and add 3-4 drops of water. Observe a vigorous reaction with precipitation of white lanthanum hydroxide. Add a few drops of nitric acid. Write down the equations for the reactions. Note the amorphous state of the precipitated lanthanum hydroxide $La(OH)_3$.

B. Reaction of a lanthanum salt with alkali

Procedure. Place 3-4 drops of a lanthanum salt solution in a test tube and add an equal volume of 2 *N* alkali solution. Divide the precipitate into two clean test tubes. Add excess alkali to one of them: does the precipitated lanthanum hydroxide dissolve? Add 2 *N* nitric acid to the other test tube. What is the character of lanthanum hydroxide? Write down the equations for the reactions conducted.

2. Preparing Sparingly Soluble Lanthanum Salts

Procedure. Place 3-4 drops of a lanthanum salt solution into each of the three test tubes and add 2-3 drops of a sodium phosphate solution to the first test tube, an equal volume of 1 *N* oxalic acid solution to the second, and 1-2 drops of sodium fluoride to the third test tube. Write down the equations for the reactions.

3. Preparing Cerium(III) Hydroxide and Its Oxidation

Procedure. Place 3-4 drops of a cerium(III) nitrate solution in a test tube and add 2 *N* alkali solution to precipitate the hydroxide. Allow the mixture to stand for 1.5-2 hours. Note the slow colour change of the precipitate $Ce(OH)_3$ due to its oxidation.

Recording the results. Write down the equations for the reaction by which cerium(III) hydroxide is prepared and oxidized with atmospheric oxygen to cerium(IV) hydroxide $CeO_2 \cdot xH_2O$. In which oxidation state is cerium more stable?

4. Peroxy Compounds of Cerium

Procedure. Prepare cerium(III) hydroxide by acting with alkali on a cerium salt. Add 2-3 drops of 3% hydrogen peroxide solution and observe a colour change of the precipitate. Add another 2-3 drops of 30% hydrogen peroxide and observe a further change in the precipitate colour which is due to formation of the peroxy compound of the $Ce(OOH)_n(OH)_{4-n}$ type with substitution of the hydroxyl groups in $Ce(OH)_4$ by the peroxy groups to form finally $Ce(OOH)_4$. Write down the equations for the reactions.

5. Reduction of Cerium(IV) Salt

Procedure. Add 0.2 *N* potassium iodide solution to a cerium(IV) nitrate solution. Observe the reaction. Write down the equation for the reaction.

25 Elements of Subgroup IIA

QUESTIONS AND PROBLEMS

1. Write down the electron formulas for the atoms of beryllium, magnesium, and the alkaline earth metals.
(a) What valence can the atoms of these elements have in their ground states?
(b) How do the properties of their hydroxides change? Explain your answer.
2. The ions of the alkaline earth metals have a weaker tendency to formation of complexes than the ions of the elements in the zinc subgroup. Explain this phenomenon.
3. Why cannot burning magnesium be extinguished with water? Write down the corresponding reaction equations.

4. Excess sodium hydroxide solution is added to a solution containing salts of calcium, beryllium and magnesium. Write down the equations for all the reactions. What substance is precipitated? What ions remain in the solution?
5. Which salt, $Be(NO_3)_2$ or $Mg(NO_3)_2$, is hydrolyzed stronger under the same conditions? Explain your answer. Write down the ionic equation for the hydrolysis of this salt. In what direction will the equilibrium be shifted if acid or soda is added?
6. Using the solubility product rule explain why $Mg(OH)_2$ is better soluble in hydrochloric acid than in ammonium chloride.
7. Explain why calcium carbonate does not precipitate when carbon dioxide is passed through calcium chloride or calcium nitrate solution. Why is calcium carbonate precipitated when carbon dioxide is passed through lime water?
8. The presence of what compounds accounts for hardness of water?
9. How can hardness of water be removed?
10. A solution contains Ca^{2+} and Ba^{2+} ions. By which reagent can these ions be precipitated? Write down the equations for the reactions.
11. What substance precipitates first when a dilute solution of sodium sulphate is added, drop after drop, to a solution containing Ca^{2+} and Ba^{2+} ions in equal concentrations? In what sequence will these ions precipitate from the solution if a dilute ammonium oxalate $(NH_4)_2C_2O_4$ solution is added?
12. Complete the following:

(a) $Ba(OH)_2 + H_2O_2 =$ (b) $BaO_2 + H_2SO_4 =$ (c) $BaO_2 + H_2O =$

To which class of chemical compounds does barium peroxide belong according to the above reaction?
13. Complete the following:

(a) $BaO_2 + FeSO_4 + H_2SO_4 =$
(b) $BaO_2 + Cr_2(SO_4)_3 + NaOH =$
(c) $BaO_2 + HgCl_2 = Hg + \ldots$

Does barium peroxide act as an oxidant or reductant in these reactions?
14. Complete the following reaction equations and indicate the oxidant and reductant in each of them:

(a) $CaH_2 + H_2O = Ca(OH)_2 + \ldots$ (b) $BaH_2 + CO_2 = C + \ldots$

Examples of Multiple-choice Questions

1. Indicate the type of orbital hybridization in the atom of Be in molecule of $BeCl_2$.
(1) sp^3; (2) sp^2; (3) s^2p^2; (4) spd^2; (5) *none*.
2. In which of the following solutions will $Be(OH)_2$ dissolve?
(1) KCl; (2) $(NH_4)_2SO_4$; (3) KOH excess; (4) HCl; (5) Na_2SO_4.
3. What silver compound will be obtained in the following reaction:

$BaO_2 + H_2SO_4 + Ag_2O = BaSO_4 + \ldots$

(1) Ag_2SO_4; (2) Ag; (3) Ag_2O_2; (4) AgOH; (5) Ag_2S.
4. What substance is formed by the action of excess alkali on beryllium sulphate?
(1) $Be(OH)_2$; (2) BeS; (3) $Na_2[Be(OH)_4]$; (4) $(BeOH)_2SO_4$; (5) BeO.
5. Indicate the number of molecules of sulphuric acid that take part in the following reaction:

$BaO_2 + KClO_4 + H_2SO_4 = KCl + \ldots$

(1) 8; (2) 4; (3) 1; (4) 2; (5) 10.

EXPERIMENT 60. BERYLLIUM. MAGNESIUM

Apparatus and reagents

Microscope. Crucible. Forceps. Abrasive paper. Magnesium ribbon. Litmus, neutral. Phenolphthalein. Solutions: hydrochloric acid, 2 *N*; nitric acid, 2 *N*; sodium hydroxide, 2 *N*; ammonia solution, 1 *N*, 1 *N* saturated with ammonium chloride; beryllium chloride, 0.5 *N*; magnesium chloride, 0.5 *N*; ammonium chloride, 2 *N*; sodium carbonate, 0.5 *N*; sodium hydrogen phosphate, 0.5 *N*.

1. Beryllium Hydroxide and Its Properties

Procedure. Place 3-4 drops of a beryllium salt solution into each of the two test tubes and add an alkali solution to precipitate beryllium hydroxide. Test the action of hydrochloric acid and excess alkali solution on the obtained hydroxide.

Recording the results. Draw your conclusion on the properties of beryllium hydroxide and write down the equation for its dissociation. Write down the equations for the reactions by which beryllium hydroxide is prepared and by which it reacts with acid and alkali, bearing in mind that the complex ion $[Be(OH)_4]^{2-}$ is formed.

2. Hydrolysis of Beryllium Salts

Procedure. Place 5-6 drops of a neutral litmus solution into a test tube and add an equal volume of beryllium chloride solution. How does the litmus colour change? Why? Write down the equation for the corresponding reaction.

3. Reaction of Magnesium with Water

Procedure. Clean the surface of a piece of magnesium ribbon 1-2 cm long from the oxide film using abrasive paper. Place 6-7 drops of distilled water and the cleaned magnesium ribbon in a test tube. Note the absence of reaction at room temperature. Heat the test tube over a small flame of the burner and observe the reaction. Add a drop of phenolphthalein solution to the test tube and observe a colour change. The formation of which ions accounts for the colour of phenolphthalein? Write down the equation for the reaction between magnesium and water with heating.

4. Reaction of Magnesium with Acids

Procedure. Place a piece of magnesium ribbon into each of the two test tubes. Add a few drops of 2 *N* hydrochloric acid solution to the first, and an equal volume of 2 *N* nitric acid solution to the second test tube.

Recording the results. What changes occur to magnesium? What gas is liberated (a) during the reaction of magnesium with hydrochloric acid, and (b) with nitric acid? Write down the reaction equations.

5. Preparing Magnesium Oxide and Its Reaction with Water

Procedure. Using forceps, take a magnesium ribbon 2-3 cm long and light it in the flame of the burner. As soon as the magnesium takes flame, hold it over a crucible. Drop the obtained magnesium oxide into the crucible and add a few drops of distilled water. Stir the mixture using a glass rod and transfer it into a test tube. Explain the turbidity of the liquid. Prove experimentally the formation of $Mg(OH)_2$ in the solution by adding a drop of phenolphthalein.

Write down the equations for the reactions by which the oxide of magnesium is formed during its burning, and for the reaction of the magnesium oxide with water.

6. Preparing Magnesium Hydroxide and Its Dissolution in Acids and Ammonium Salts

Procedure. Place 3 drops of a magnesium salt into each of two test tubes and add 4 drops of sodium hydroxide solution to each test tube. Add, drop by drop, 2 *N* hydrochloric acid solution to one test tube and stir the mixture using a glass rod until the precipitate is dissolved completely. Count the number of drops of the acid added. Dissolve the precipitated magnesium hydroxide in the other test tube in a similar way in 2 *N* ammonium chloride solution. Which reagent is required in a greater volume to dissolve the precipitate?

Recording the results. Write down the equations for the reactions by which magnesium hydroxide is prepared and by which it is dissolved in acid and in ammonium salt solutions.

Using the solubility product rule, explain dissolution of magnesium hydroxide in ammonium chloride and in hydrochloric acid. Which reagent dissolves the hydroxide easier, hydrochloric acid or ammonium chloride? Explain. Does magnesium hydroxide dissolve if (a) $(NH_4)_2SO_4$ or (b) KCl is added?

7. Sparingly Soluble Magnesium Salts

A. Preparing basic magnesium carbonate

Procedure. Place 2-3 drops of a magnesium salt in a test tube and add a soda solution to precipitate basic magnesium carbonate. Observe liberation of gas. Test the action of hydrochloric acid on the precipitate. Write down the equations for the reactions by which basic magnesium carbonate is prepared and dissolved in acid.

Fig. 43.
Crystals of $MgNH_4PO_4 \cdot 6H_2O$ as viewed in a microscope

B. Microcrystalloscopic reaction for preparing ammonium magnesium phosphate

Procedure. Place a drop of a magnesium salt solution on a glass slide and add a drop of 1 *N* ammonia solution saturated with ammonium chloride. Mix the liquids using a glass rod: the resultant solution should be clear. Add a crystal of sodium hydrogen phosphate Na_2HPO_4. Examine the crystals of the prepared double salt $MgNH_4PO_4 \cdot 6H_2O$ under a microscope (Fig. 43). Remove the slide from the microscope and add a drop of hydrochloric acid. Observe dissolution of the precipitate. Write down the reaction equation. Describe the test done. Draw a sketch of the prepared crystals.

EXPERIMENT 61. ALKALINE EARTH METALS

Apparatus and reagents

Muffle furnace.
Desiccator. Microscope. Crucible tongs.
Forceps. Crucible. Clay triangle.
Slide.
Apparatus for preparing CO_2.
Platinum loop soldered into a glass rod. Marbel. Calcium.
Phenolphthalein. Barium peroxide.
Manganese dioxide. Lime water.
Solutions: hydrochloric acid, 2 *N*; density 1.19 g/cm³; sulphuric acid, 2 *N*; acetic acid, 2 *N*; sodium hydroxide, 2 *N*; calcium chloride, 0.5 *N*, saturated; strontium chloride, 0.5 *N*, saturated; barium chloride, 0.5 *N*, saturated; sodium carbonate, 0.5 *N*; sodium sulphate, 0.5 *N*; ammonium oxalate, 0.5 *N*; sodium hydrogen phosphate, 0.5 *N*; potassium chromate, 0.5 *N*; potassium iodide, 0.1 *N*; silver nitrate, 0.1 *N*.

1. Reaction of Calcium with Water

Procedure. Fill a test tube with distilled water to 1/3 its capacity and add a small grain of calcium (using forceps). What gas is evolved? Why does water turn cloudy? Prove formation of alkali in the solution by adding a drop of phenolphthalein. Observe the reaction. Explain your observations.

Recording the results. Write down the equation for the reaction between calcium and water. Indicate the oxidant and the reductant in this reaction.

2. Preparing Calcium Oxide and Calcium Hydroxide

Procedure. Place a piece of marble into a test tube and add a few drops of water. Does the reaction occur? Add a drop of phenolphthalein. Does the solution turn red?

Place another piece of marble into a crucible and calcine in a muffle furnace at about 910°C for 20-25 minutes. Using crucible tongs, transfer the crucible into a desiccator and cool to room temperature. Add 1-2 drops of distilled water to the cooled calcium oxide and observe the reaction. Add another 8-10 drops of water, stir the formed calcium hydroxide (slaked lime) and allow the mixture to stand. Transfer 2-3 drops of the obtained solution into a test tube using a pipette and add a drop of phenolphthalein. What is the reaction of the medium? Is calcium hydroxide soluble in water? Write down the equations for the thermal decomposition of calcium carbonate and for the reaction of calcium oxide with water. What is the name of an aqueous solution of calcium hydroxide?

3. Calcium Carbonate and Calcium Hydrogen Carbonate

A. Preparing calcium carbonate and hydrogen carbonate

Procedure. Half fill a test tube with lime water and pass carbon dioxide through it. Observe precipitation of calcium carbonate. Continue passing carbon dioxide through the solution until the precipitate dissolves due to formation of the soluble hydrogen carbonate. What is the name of the solution containing this salt? Save the solution for test 3*B*.

Recording the results. Describe the reactions observed, and write down the equations (a) for the reaction between carbon dioxide and lime water with formation of calcium carbonate, and (b) for dissolution of calcium carbonate by the action of carbon dioxide and water with formation of the hydrogen carbonate.

B. Removal of temporary hardness of water

Procedure. Using a pipette, transfer half of the solution prepared in the previous test into a test tube or a microflask. Fix it in the stand in an inclined position and heat carefully to boiling: calcium carbonate precipitates. Precipitate calcium carbonate from the remaining portion of the solution by adding 1-2 drops of sodium hydroxide solution. Describe your observations and write down the equations for the reaction by which the hydrogen carbonate is decomposed by boiling, and by the interaction with alkali.

4. Carbonates of the Alkaline Earth Metals

Procedure. Precipitate carbonates of calcium, strontium, and barium by reacting 3-4 drops of the corresponding salt with sodium carbonate solution. Try the action of hydrochloric acid on the obtained carbonates. Add the acid carefully, drop by drop. Write down the equations for the corresponding reactions. Characterize the solubility of the carbonates in the acid.

5. Sulphates of the Alkaline Earth Metals

A. Preparing sulphates of calcium, strontium, and barium

Procedure. Place 2-3 drops of a calcium salt solution into the first test tube, of a strontium salt solution into the second test tube, and of a barium salt solution into the third test tube. Add 3-4 drops of sodium sulphate solution to each test tube: observe the reaction. Note the different rate of precipitation of barium sulphate and calcium sulphate. How can this difference be explained? Test the effect of hydrochloric acid on the prepared sulphates.

Recording the results. Write down the equations for the reactions by which sulphates of calcium, strontium, and barium are prepared; write down the expression of the solubility product for barium sulphate and barium carbonate. Using the solubility product rule, explain why barium carbonate dissolves in dilute hydrochloric acid while barium sulphate does not.

B. Comparison of calcium sulphate and calcium carbonate solubilities

Procedure. Prepare calcium sulphate by adding 5-6 drops of sodium sulphate solution to 3-4 drops of calcium chloride. Allow the solution to settle and transfer a portion into a clean test tube. Make sure that precipitation is complete by adding one more drop of the sodium sulphate solution. Add a few drops of sodium carbonate solution to the clear test solution and observe the reaction.

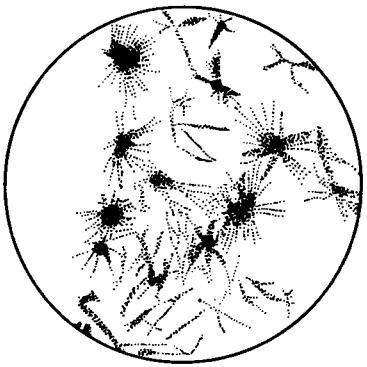


Fig. 44.
Crystals of $CaSO_4 \cdot 2H_2O$ as viewed in a microscope

Recording the results. Use the solubility product rule (and consult the table of solubility products) to explain why the solution, after $CaSO_4$ has been precipitated from it, gives another precipitate if CO_3^{2+} ions are added.

C. Microcrystalloscopic reaction for preparing calcium sulphate

Procedure. Place a drop of a calcium chloride solution on a glass slide and add a drop of 2 *N* sulphuric acid solution. Wait till the solution turns cloudy and use a microscope to examine the crystals of $CaSO_4 \cdot 2H_2O$ (Fig. 44).

Recording the results. Write down the ionic and molecular equations for the reaction and draw sketches of the crystals.

6. Oxalates of the Alkaline Earth Metals

Procedure. Obtain the precipitates of calcium, strontium and barium oxalates by reacting the relevant salts (3-4 drops) with equal volumes of ammonium oxalate. Test the effect of hydrochloric acid on the oxalates.

Recording the results. Write down the equations for the reactions by which the oxalates of the alkaline earth metals are prepared and dissolved in HCl.

7. Chromates of the Alkaline Earth Metals

Procedure. Place 3-4 drops of calcium, strontium and barium salt solutions into three separate test tubes and add 4-5 drops of potassium chromate solution to each solution. Chromates of which metals are thus precipitated? Note their colour. Test the action of acetic acid on the chromates obtained.

Prepare barium chromate again and try the action of hydrochloric acid on it. Observe the reaction.

Recording the results. Write down the equations for the reactions by which the chromates of barium, calcium, and strontium are prepared and dissolved in the acid. Explain why strontium chromate dissolves in acetic acid, while barium chromate is almost insoluble in it, but is soluble in hydrochloric acid. The chromate of which metal is most soluble?

8. Barium Peroxide

A. Oxidizing properties of barium peroxide

Procedure. Place 3-4 microspatulas of barium peroxide in a porcelain crucible and add a small portion (on the tip of the spatula) of powdered manganese dioxide. Mix thoroughly, using a glass rod, place the crucible in a clay triangle over a burner and heat to fuse the mixture. Cool the melt and note its colour which is specific for manganate. Write down the equation for the reaction.

B. Reducing properties of barium peroxide

Procedure. Place 6-7 drops of a silver nitrate solution in a test tube and add a small quantity of powdered barium peroxide. Observe evolution of gas and precipitation of silver metal. What gas is liberated? Write down the reaction equation.

9. Colouration of Flame by Salts of the Alkaline Earth Metals

Procedure. Dip a platinum loop (or a thin porcelain rod) into concentrated hydrochloric acid and introduce it into the flame of the burner to calcine and remove contaminants. The clean wire should not colour the flame.

Dip the clean platinum loop into a saturated barium chloride solution and introduce into the flame again. Note the colour of the flame. Repeat the experiment using saturated solutions of strontium chloride and calcium chloride. Before each new test, rinse the wire in concentrated hydrochloric acid and calcine. Describe your observations.

EXPERIMENT 62. DETERMINING HARDNESS OF WATER

Apparatus and reagents

Burettes, 25-ml.
Pipettes, 50- and 100-ml.
Erlenmeyer flasks, 250-ml. Funnels for burettes. Indicators: methyl orange; eriochrome black T, 0.2% solution in alcohol; or chromogen black, ET-OC (dissolve 0.5 g of the preparation in 10 ml of buffer solution and dilute with alcohol to 100 ml). Solutions: hydrochloric acid, 0.1 *N*, standard; buffer solution (dissolve 20 g of chemically pure ammonium chloride in distilled water, add 100 ml of a 25% ammonium hydroxide solution, and dilute with distilled water adding it to the mark in a 1000-ml flask); EDTA, 0.02 *N*, standard; (dissolve 3.7224 g of EDTA in distilled water in a 1000-ml measuring flask and add water to the mark).

Hardness of water is due to the presence of soluble salts of calcium and magnesium, hydrogen carbonates, chlorides and sulphates. Temporary (removable) and permanent hardness of water are distinguished. Temporary hardness depends on the presence of soluble calcium and magnesium hydrogen carbonates. When water is boiled, the hydrogen carbonates are converted into sparingly soluble carbonates:

$$Ca(HCO_3)_2 = CaCO_3 + CO_2 + H_2O; \quad Mg(HCO_3)_2 = MgCO_3 + CO_2 + H_2O$$

Temporary hardness of water is thus removable. The sum of temporary and permanent hardness is the total hardness of water. Hardness is expressed in millimoles of equivalent ions of Ca^{2+} and Mg^{2+} per litre of water. Soft water contains less than 4 mmol equiv/l, water of medium hardness contains from 4 to 8, and hard water contains from 8 to 12 mmol equiv/l.

A. Determining temporary hardness

Since water containing hydrogen carbonates of calcium and magnesium reacts alkaline (why?), its hardness can be determined by direct titration of water with hydrochloric acid in the presence of methyl orange indicator.

Procedure. Using a pipette, transfer 50-100 ml of test water into an Erlenmeyer flask for titration. Add 2-3 drops of methyl orange. Pour 0.1 *N* standard solution of hydrochloric acid into a burette. Adjust the liquid level at zero reading and add hydrochloric acid, drop by drop, to the water until the yellow solution turns orange-pink. Determine the volume of hydrochloric acid spent for titration and tabulate the data. Repeat the titration two times, adjusting the acid level in the burette at zero before each titration. Also rinse the titration flask before each determination. The experimental

data should not differ by more than 0.05 ml. Fill in the table as shown below

Test No.	Volume of pipette (volume of H_2O) V_1, ml	HCl spent for titration, ml	Mean volume of HCl, V_2, ml	HCl normality, N_{HCl}

Temporary hardness of water (in mmol equiv/l) is calculated by the formula

$$\text{Temporary hardness} = \frac{N_{HCl} V_{2HCl} \times 1000}{V_{1H_2O}}$$

B. Determining the total hardness of water

At present, the hardness of water is determined complexonometrically, using EDTA.

Procedure. Place a standard EDTA solution (0.02 *N*) into a burette. Measure out a volume of test water with a pipette and transfer it into a conical titration flask. Add distilled water to make 100 ml (use a measuring cylinder). Add 5 ml of buffer ($NH_3 + H_2O + + NH_4Cl$) to maintain the pH of the solution in the range from 9 to 10 and 2-3 drops of eriochrome black indicator. The solution turns red. Stir the solution and titrate immediately with the EDTA solution from the burette until the red solution turns blue. Repeat the titration three times, as in test *A*. Write down the results of the experiment into the table.

Calculate the total hardness of water (in mmol equiv/l) from the following formula:

$$\text{Total hardness} = \frac{N_{EDTA} V_{2EDTA} \times 1000}{V_{1H_2O}}$$

Calculate permanent hardness:

Permanent hardness = total hardness — temporary hardness

What is the hardness of the water used in this test?

26 Elements of Subgroup IA

QUESTIONS AND PROBLEMS

1. Write down the electron structures for the potassium and cesium atoms. Which of these elements is a stronger reductant? Why?
2. How do the electron structures of the atoms of the alkali metals differ from those of the elements belonging to the copper subgroup? How do the properties

of the hydroxides of these elements and their complexing power depend on their electron structures?
3. Explain the lower activity of lithium as compared with potassium and sodium, remembering that its normal electrode potential is the lowest (—3.01 V).
4. Write down the equations for the reactions of (a) K_2O and (b) K_2O_2 with water.
5. How do the reactions of lithium and sodium with oxygen differ? Write down the equations for the reactions.
6. How can potassium metal and potassium hydroxide be prepared from potassium chloride? Give schemes for the corresponding reactions.
7. Which of the following gases, H_2S, H_2, Cl_2, or CO_2 will be absorbed by sodium hydroxide solution? Write down the equations for the corresponding reactions.
8. What is the reaction of the medium in the solutions of the following salts: KNO_3, K_2S, KCH_3COO? Write down the ionic equations for the hydrolysis of the corresponding salts.
9. Write down the equations for the reactions by which the following conversions can be realized:

$Na \rightarrow NaOH \rightarrow Na_2CO_3 \rightarrow NaCH_3COO$.

10. Complete the following:

(a) $Na_2O_2 + KI + H_2SO_4 =$ (b) $Na_2O_2 + Fe(OH)_2 + H_2O =$
(c) $Na_2O_2 + KMnO_4 + H_2SO_4 =$

Does sodium peroxide act as an oxidant or reductant in these reactions?
11. Write down the equation for the reaction by which lithium hydride is prepared. How do the hydrides of the alkali and alkaline earth metals differ from hydrides of nonmetals with respect to their valence bonds and physical properties?
12. Complete the following equations and indicate the oxidant and the reductant in each reaction

a) $Na + H_2 =$ (b) $Li_3N + H_2 = LiH + \ldots$ (c) $NaH + H_2O = H_2 + \ldots$

Examples of Multiple-choice Questions

1. Which salts of the alkali metals are sparingly soluble?
(1) Li_3PO_4; (2) Na_2S; (3) K_2CO_3; (4) $CsNO_3$; (5) $KClO_4$.
2. Which salts of the alkali metals are practically not hydrolyzed?
(1) K_2CO_3; (2) $NaNO_3$; (3) LiCl; (4) KCH_3COO; (5) Na_2S.
3. In which of the following reactions does Na_2O_2 demonstrate its oxidizing properties?
(1) $Na_2O_2 + KI$; (2) $Na_2O_2 + Fe(OH)_2$; (3) $Na_2O_2 + KMnO_4$; (4) $Na_2O_2 + + H_2O$; (5) $Na_2O_2 + H_2SO_4$.
4. Which of the following is a stronger base?
(1) LiOH; (2) NaOH; (3) KOH; (4) RbOH; (5) CsOH.
5. Indicate the substance that is liberated (and in what quantity) at the cathode during electrolysis of an aqueous solution containing 11.7 g of sodium chloride:
(1) Na, 4.6 g; (2) Cl, 7.1 g; (3) H, 0.2 g; (4) O, 1.6 g.

EXPERIMENT 63. ALKALI METALS

Apparatus and reagents

Microscope.
Platinum loop soldered in a glass rod.
Glass prism with indigo blue solution.
Crucible. Forceps. Clay triangle.
Sodium. Sodium peroxide. Sodium carbonate. Sodium bicarbonate.

Chromium sulphate. Potassium chloride.
Litmus, neutral. Phenolphthalein.
Solutions: potassium permanganate, 0.05 *N*;
potassium hexahydroxystibate(V), saturated; potassium chloride, saturated; sodium chloride, saturated; lithium sulphate, saturated; sodium carbonate, saturated. Specific reagent for K^+ ion (dissolve 2 g of $NaNO_2$, 0.9 g of $Cu(CH_3COO)_2$, 1.7 g of $Pb(CH_3COO)_2$ and 0.2 ml of a 30% solution of acetic acid in 1.5 ml of water).

1. Sodium Peroxide

A. Reaction of sodium peroxide with water

Procedure. Place a small quantity of sodium peroxide into a test tube using a spatula and add 8-10 drops of distilled water. Stir the mixture using a glass rod. Prove the presence of alkali in the obtained solution by adding a drop of phenolphthalein solution. Write down the equation for the reaction between sodium peroxide and water.

B. Oxidizing properties of sodium peroxide

Procedure. Place 3 microspatulas of sodium peroxide, 2 microspatulas of sodium carbonate, and a small quantity (at the tip of the microspatula) of powdered chromium sulphate into a crucible. Mix thoroughly using a glass rod, and put the crucible in a clay triangle. Heat over a burner to melt the mixture. Cool the crucible in air and add 8-10 drops of distilled water. Stir with a glass rod, allow the mixture to settle, and pour off the liquid into a test tube. Note the colour of the formed Na_2CrO_4. Write down the equation for the reaction between sodium peroxide and chromium sulphate in the presence of Na_2CO_3, bearing in mind that carbon dioxide is also produced in the reaction.

C. Reducing properties of sodium peroxide

Procedure. Place 4-5 drops of potassium permanganate solution into a test tube and add a microspatula of sodium peroxide powder. Mix the substances and observe evolution of gas and precipitation of a brown substance. Write down the equation for the reaction.

2. Sodium Carbonate and Sodium Hydrogen Carbonate

A. Reaction of the medium in solutions of sodium carbonate and hydrogen carbonate

Procedure. Place 6-7 drops of distilled water in each of the three test tubes and add equal volumes of neutral litmus solution to each test tube. Add a microspatula of sodium carbonate crystals to the

first test tube, and the same amount of sodium hydrogen carbonate to the second test tube. Keep the third test tube for comparison. Stir the solutions using glass rods. Compare the colour of litmus in solutions of the salts with the colour in the third test tube. Save all three test tubes as reference for the next test.

Recording the results. Answer the questions: what is the medium (and why) in the following solutions:

(a) sodium carbonate solution;

(b) sodium hydrogen carbonate solution.

Write down the ionic and molecular equations for the reactions. Why is the litmus colour different in solutions of the salts? Explain your answer.

B. Thermal decomposition of sodium hydrogen carbonate

Procedure. Place 3-4 microspatulas of sodium hydrogen carbonate powder in a crucible, place the crucible in a clay triangle and calcine over a flame of the burner for 10-15 minutes. Cool the crucible in air, add 12-14 drops of distilled water, stir with a glass rod, and pour the solution into two test tubes. Prove the presence of a salt of carbonic acid in the solution. To do so, add 3-4 drops of 2 *N* hydrochloric acid solution to one test tube and observe bubbling. What gas is evolved? Add an equal amount of a neutral litmus solution to the other test tube. Compare the litmus colour in this solution with the colour of reference solutions prepared in the previous test. Decide which salt, carbonate or hydrocarbonate, is present in the solution (by the colour of litmus). Describe the work done. Write down the equation for the thermal decomposition of sodium hydrogen carbonate. This reaction is used for industrial manufacture of soda.

3. Sparingly Soluble Salts of the Alkali Metals

A. Microcrystalloscopic reaction for the sodium ion

(preparing crystals of sodium hexahydroxystibate(V) $Na[Sb(OH)_6]$).

Procedure. Place a drop of a saturated potassium hexahydroxystibate(V) solution on a slide and introduce a crystal of a sodium salt using a glass rod. Examine the formed crystals of $Na[Sb(OH)_6]$ under a microscope. Depending on the rate of crystallization, the crystals may be prisms or lenses; cross-shaped aggregations are also common (Fig. 45). Write down the equation for the reaction and draw sketches of the crystals.

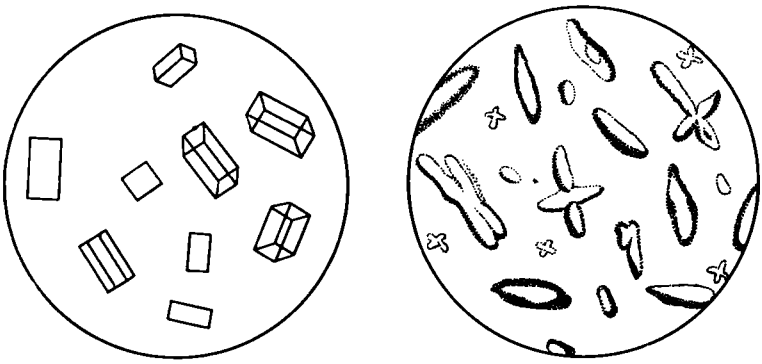


Fig. 45.
Crystals of $Na[Sb[OH]_6]$ prepared with slow (a) and rapid (b) crystallization as viewed in microscope

B. Microcrystalloscopic reaction for the potassium ion

(preparing crystals of $K_2Pb[Cu(NO_2)_6]$)

Procedure. Place a drop of the specific reagent on a slide. The composition of the reagent can be expressed by the formula $Na_2Pb[Cu(NO_2)_6]$. Introduce a grain of a potassium salt into it. View the formed crystals under a microscope. Observe their growth. The crystals are black cubes (Fig. 46). The composition of the crystals is $2KNO_2 \cdot Pb(NO_2)_2 \cdot Cu(NO_2)_2$ or $K_2Pb[Cu(NO_2)_6]$. Draw the sketches of the crystals.

C. Preparing lithium carbonate

Procedure. Place 4-5 drops of a lithium sulphate solution in a test tube and add an equal volume of a sodium carbonate solution. Heat

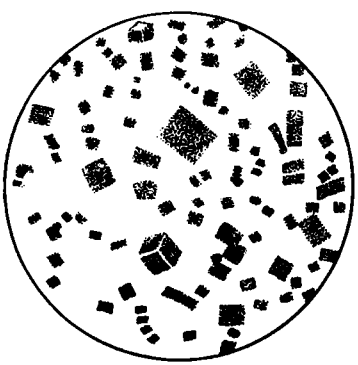


Fig. 46.
Crystals of $K_2Pb[Cu(NO_2)_6]$ as viewed in a microscope

the test tube in a boiling water bath and observe first cloudiness and then precipitation of lithium carbonate. Write down the reaction equation.

4. Colouration of Flame with Alkali Metal Salts

Procedure. Dip a platinum loop into a saturated solution of potassium chloride and put into the flame of a burner. Note the colour of the flame.

Minutest admixtures of sodium colour the flame yellow which often masks the violet flame of potassium. Therefore, use a glass prism with indigo blue solution to regard the flame: the solution absorbs the yellow light completely.

Repeat the experiment using saturated solutions of lithium sulphate and sodium chloride. Clean the wire thoroughly before each experiment by dipping it into concentrated hydrochloric acid and calcining in the flame.

EXPERIMENT 64. SYNTHESIS OF SODIUM CARBONATE AND SODIUM HYDROGEN CARBONATE

Apparatus and reagents	
Cylinder with CO_2, or Kipp's generator. 100-150-ml cylinder with a stopper provided with a tube reaching the cylinder bottom.	Vacuum filtration unit. Porcelain dish. Porcelain crucibles. Sodium chloride, fine crystals. Ammonia, 10% solution. Litmus. Phenolphthalein. Methyl orange.

The industrial manufacture of sodium carbonate is based on the Solvay process (ammonia soda process). It can be illustrated by the following chemical reactions:

$$NH_3 + H_2O + CO_2 = NH_4HCO_3$$
$$NH_4HCO_3 + NaCl = NaHCO_3 + NH_4Cl$$
$$2NaHCO_3 \xrightarrow{t} Na_2CO_3 + CO_2 + H_2O$$

Practical irreversibility of the second reaction is due to a very low solubility of sodium hydrogen carbonate in cold water containing carbon dioxide.

A. Preparing sodium hydrogen carbonate

Procedure. Prepare 50 ml of 10% ammonia solution saturated with sodium chloride at room temperature. To do so, calculate the weight of water contained in 50 ml of the ammonia solution by its

specific gravity (Table 4 of Appendix), and the weight of sodium chloride that will dissolve in this quantity of water (from the solubility of NaCl, as specified in Table 5 of Appendix). Weigh out 2-3 g more than the calculated amount of the salt on a chemical balance and dissolve in 50 ml of 10% ammonia solution.

Filter the obtained saturated solution into a 100- or 150-ml cylinder, close it (loosely) with a cork stopper provided with a gas discharged tube (which reaches almost the cylinder bottom), and pass carbon dioxide through the solution from a compressed gas cylinder (or Kipp's generator) for 50-55 minutes (*use the hood*!). Adjust the gas flow rate so that a small pressure is created in the cylinder (the stopper should not be driven out by this pressure). Maintain the temperature of the solution at 25-26°C. If the temperature rises above 30°C, cool the cylinder in a cold water bath. Place the funnel with undissolved sodium chloride in a drying cabinet, and weigh the dry salt to calculate the yield of the product.

Separate the formed $NaHCO_3$ precipitate on a Büchner funnel, rinse with a small quantity of ice-cold water, and dry thoroughly between filter papers. Place a small quantity of the dry sodium hydrogen carbonate into a test tube, dissolve in distilled water, and test the effect of the solution on litmus, phenolphthalein, and methyl orange. What is the pH of the obtained solution (see Table 9 of Appendix)?

B. Preparing sodium carbonate

Transfer sodium hydrogen carbonate prepared in *A* in a porcelain dish and calcine carefully, with stirring, until all water is evaporated. Cool the dish containing Na_2CO_3 and weigh the prepared sodium carbonate.

Dissolve a small portion of the carbonate in distilled water and test the solution with indicators as in the case with sodium hydrogen carbonate.

Which salt, sodium carbonate or hydrogen carbonate, has a higher degree of hydrolysis? Explain your answer. Does the theory agree with practical observations?

Calculate the yield of sodium carbonate Na_2CO_3 with respect to sodium chloride. Handle the salt over to the laboratory assistant.

27 Titrimetric Determinations

EXPERIMENT 65. DETERMINING COMPOSITION OF CARBONATES BY BACK TITRATION

Apparatus and reagents

Volumetric flasks, 100-ml. Burettes, 50-ml. Pipettes, 10-ml. Erlenmeyer flasks, 50-100-ml. Fine crystalline powders of Na_2CO_3, $Na_2CO_3 \cdot 10\,H_2O$, and $NaHCO_3$. Phenolphthalein.

Procedure. Obtain a carbonate (Na_2CO_3, $Na_2CO_3 \cdot 10H_2O$ or $NaHCO_3$) from the instructor. Identify the salt. To do so, act as follows. Dissolve the unknown salt in excess standard hydrochloric acid, determine the excess by back titration with a standard alkali solution, and establish the composition of the salt from the amount of acid spent for dissolution of the salt. Ammonium salts can be analyzed in a similar way by dissolving them in standard alkali solution and conducting back titration with a standard acid solution.

Weigh out about 2 g of the obtained salt on a chemical balance to an accuracy of 0.02 g. Transfer the salt through a dry funnel into a 100-ml volumetric flask and rinse the funnel (without removing it from the flask) with a small amount (5-10 ml) of distilled water.

Place 1 *N* standard hydrochloric acid solution into a 50-ml burette, and adjust the liquid level at zero (by the bottom of the meniscus). Put the volumetric flask beneath the burette and add, by small portions, 45 ml of the acid solution with stirring it (by rotating the flask) after adding each new portion. The acid should be added gradually and with precautions because the reaction is accompanied with liberation of carbon dioxide and the liquid can be expelled from the flask:

$$CO_3^{2-} + 2H^+ = CO_2 + H_2O \quad \text{or} \quad HCO_3^- + H^+ = CO_2 + H_2O$$

After the acid has been added, continue shaking the flask to complete dissolution of the salt. Then add distilled water to the mark, close the flask with a stopper and stir the solution thoroughly. Rinse a pipette with the obtained solution and transfer 10-ml portions of the solution into each of the four flasks using the pipette.

Place 0.1 *N* standard sodium hydroxide solution in a clean burette and adjust the liquid level at zero. Add two drops of phenolphthalein to one flask and then add, from the burette, 0.5-1 ml portions of the alkali solution. Stop adding the alkali when the solution turns red after addition of a next new portion and the colour persists for 1-2 minutes. Note the volume of the alkali spent for

this tentative titration. Carry out a more accurate titration of the solution in the remaining three flasks, adding the alkali by drops at the end of titration.

Recording the results. Write down the findings:

Weight of glass slide, g_1, in g.

Weight of the slide with salt, g_2, in g.

Weight of salt, $g = g_2 - g_1$, in g.

Volume of flask with test salt solution, 100 ml.

Volume of pipette, 10 ml.

Volume of 1 N hydrochloric acid solution taken for dissolution of the salt, 45 ml.

Volume of 0.1 N sodium hydroxide solution spent for back titration of 10 ml of the test solution: V_1, V_2, V_3

$$V_{mean} = (V_1 + V_2 + V_3)/3$$

Calculate the volume of the alkali, in ml, which is necessary to neutralize the excess hydrochloric acid in the 100-ml flask after dissolution of the salt:

$$V_{0.1N,\ NaOH} = V_{mean} \times 100/10$$

The volume of 1 N solution is 10 times smaller: $V_{1N,\ NaOH} = V_{mean}$.

According to the law of equivalent weights, excess of a 1 N acid solution in the flask is equal to the volume of 1 N alkali solution spent for back titration, i.e. V_{mean}. It follows that of the 45 ml of 1 N hydrochloric acid taken for the reaction with the test salt, $(45 - V_{mean})$ ml were only spent, which contain $1 \cdot (45 - V_{mean})/1000$ equivalent weights. According to the law of equivalent proportions, the same quantity of equivalents is contained in the salt sample taken for the analysis. The mass of the dissolved salt can thus be calculated from the formula

$$m_{salt} = \frac{45 - V_{mean}}{1000} E$$

where E is the equivalent of the salt.

Equivalent masses of Na_2CO_3, $Na_2CO_3 \cdot 10H_2O$ and $NaHCO_3$ are 53, 143, and 84 g, respectively. (Check your calculations.)

Substitute said values of equivalent masses into the last formula. The salt obtained from the instructor, with the calculated mass m_{salt}, weighs g grams.

EXPERIMENT 66. DETERMINING CONCENTRATION OF SODIUM CHLORIDE BY ARGENTOMETRIC TITRATION

Apparatus and reagents	Solutions: silver nitrate, 0.1 N, standard; sodium chloride, 0.5 N, standard; potassium chromate, saturated.
Volumetric flask, 50-ml. Burette, 10-ml. Pipette, 5-ml.	

The concentration of some salts in a solution can be determined from the exchange reaction in which sparingly soluble precipitates are formed during titration. For example, the chlorides (or bromides) of metals can be determined by precipitating silver halides:

$$Cl^- + Ag^+ = AgCl\downarrow$$

The halide solution is titrated with silver nitrate solution (see Experiment 12) whose concentration is known. A drop of a saturated potassium chromate solution K_2CrO_4 is added to the halide solution as an indicator to determine the titration end point. Potassium chromate reacts with silver nitrate to give a sparingly soluble dark red salt Ag_2CrO_4. But silver chromate is much more soluble than silver chloride; and silver chromate begins precipitating only after practically complete precipitation of the chloride ions. The white precipitate turns brown, which indicates the end of the reaction between sodium chloride and silver nitrate*.

Procedure. Obtain a sample of sodium chloride solution from the instructor in a 50-ml volumetric flask and add distilled water (from a wash bottle) to the mark. Add water by small portions, shaking the flask after adding each new portion. Add the last drops of water from a pipette, until the bottom of the meniscus aligns with the mark. Close the flask tightly and mix the solution thoroughly by overturning the flask.

Rinse a 10-ml burette with a small portion of a standard 0.1 *N* silver nitrate solution. Fix the burette in the stand and fill, through a funnel, with the silver nitrate solution slightly above the zero mark. (The burette tip should be filled as well.) Release the solution excess through the lower end of the burette to adjust the level at zero.

Place 5 ml of the prepared sodium chloride solution into a 50-ml conical flask using a pipette and add about an equal volume of water from a wash bottle. Add a drop of a saturated potassium chromate solution (indicator). Carry out tentative titration. To that end, add from a burette small portions (0.5 ml) of silver nitrate solution to the flask containing sodium chloride solution. Stir the liquid rotating the flask. Establish the moment when the yellow colour of the solution with the precipitate turns brownish. Stop the titration and determine the volume of the silver nitrate solution spent for titration.

Repeat the titration three times, but be more accurate: add the last portions of silver nitrate drop by drop. Wash the flask thoroughly and rinse with distilled water before each titration; adjust the silver nitrate solution level in the burette at zero.

* Waste solutions containing silver salts should be handled back to the laboratory assistant.

Recording the results. Write down the equation for the reaction. Tabulate the data as follows:

No.	Volume of sodium chloride, ml	Indicator (potassium chromate), in drops	Volume of 0.1 *N* silver nitrate solution spent for titration, ml
1	5	1	5.42
2	5	1	5.44
3	5	1	5.43
			mean 5.43

Find the mean value of the last three titration results to determine the volume of the silver nitrate solution spent for titration. The normality of the silver nitrate solution and the volumes of the reacted solutions are known. Calculate the normality of the test solution of sodium chloride and determine the salt concentration in it. Check your results by consulting the instructor.

28 Methods of Physicochemical Analysis

The methods of physicochemical analysis are based on the study of the relationship between the chemical composition and some physical properties of the system, such as its density, viscosity, solubility, boiling and melting points, etc. The results are usually expressed graphically. Experimental data for a given system are plotted in a graph showing the dependence of the properties on the composition of a given substance; the composition is plotted against the axis of abscissas and the properties against the axis of ordinates. Lines drawn through these points characterize the dependence of the properties on composition of the system and are used to establish the relation of any composition of the system to the property in question. A smooth course of the graph corresponds to a gradual variation of the factor in question (composition, temperature, pressure, etc.), which does not involve changes in the qualitative composition of the system. Sharp changes in the course of the line, or intersection of the lines indicate conversions and chemical reactions between substances. The analysis of curves and geometrical figures on the graph, showing the dependence of properties on composition, reveals the character of chemical processes occurring in the system and establishes the composition of the liquid and solid phase without their separation.

Thermal analysis is a special case of physicochemical analysis, which is very important for the study of alloys and their properties. Phase diagrams are used in this analysis. They show the dependence of the melting point on the composition.

EXPERIMENT 67. DETERMINING THE TEMPERATURE OF TRANSITION OF SODIUM SULPHATE CRYSTAL HYDRATE INTO THE ANHYDROUS SALT BY DENSITY OF SOLUTION

Apparatus and reagents

Beaker, 400-ml.
Thermometer, scale to 100°C.
Cylinder. Hydrometers (scale from 1 to 1.35 g/cm³). Sodium sulphate decahydrate $Na_2SO_4 \cdot 10H_2O$ (or anhydrous Na_2SO_4).

Procedure. Place 200 ml of distilled water in a 400-ml beaker and add, by small portions, sodium sulphate decahydrate, $Na_2SO_4 \cdot 10H_2O$, or the anhydrous salt Na_2SO_4, at room temperature. Stir the solution continuously using a glass rod. Stop adding the salt when it dissolves no longer and precipitates to the bottom. Allow the solution to stand for a few seconds. Transfer part of the solution to a cylinder and measure its density and temperature using a hydrometer and a thermometer, respectively. Write down your findings into the log-book.

Pour the solution back into the beaker, place it on an asbestos-centred gauze over a burner, and heat to 4-6°C above room temperature with stirring. When the precipitate has been dissolved, add new portions of the salt to prepare a saturated solution. Transfer a portion of the solution into a graduated cylinder and measure its density and temperature again. Proceed similarly to determine the density of saturated solutions four or five times at different temperatures (not exceeding 55°C).

At certain temperatures at the end of the experiment new portions of the salt will be unnecessary: the amount of the insoluble precipitate will increase on the beaker bottom. If this is the case, stir the solution for 5 minutes and measure the density and temperature as instructed above.

Recording the results. Fill in the following table:

Data \ Point No.	1	2	3	4	5	6	7
Temperature, °C							
Density, g/cm³							

Plot the graph showing the dependence of the density of solutions d on the temperature. The axis of abscissas is graduated into 10°C temperature intervals from zero to 60°C. The density is plotted along the axis of ordinates and each division corresponds to 0.05 g/cm³. Note that the density of saturated sodium sulphate solutions first increases with temperature, and then begins decreasing. Draw a line through the points showing increasing density, and another line through the points showing the decreasing density. The point of intersection of the lines indicates the point where the crystal hydrate converts into the anhydrous salt. Draw a vertical line from this point until it intersects the axis of abscissas: the point of intersection reads the temperature, at which this conversion occurs. This temperature is only tentative because the procedure was carried out in conditions of unstable equilibrium. Determine the accuracy of your determination knowing that the temperature at which the hydrate converts into the anhydrous salt ($Na_2SO_4 \cdot 10H_2O \rightleftarrows Na_2SO_4 + 10H_2O$) is 32.4°C.

EXPERIMENT 68. DETERMINING THE DOUBLE POINT OF CALCIUM HYDROGEN PHOSPHATE-CALCIUM DIHYDROGEN PHOSPHATE BY SOLUBILITY OF CALCIUM OXIDE IN PHOSPHORIC ACID

Apparatus and reagents	Calcium oxide. Phosphoric acid, 40% solution with respect to P_2O_5, density 1.38 g/cm³.
Beaker, 250-ml.	

Calcium phosphates are widely used in agriculture as a mineral fertilizer. Neutral, acid and basic salts are known. Each salt can be prepared at certain conditions of temperature and composition of a saturated solution from which it is precipitated. The optimum conditions for the manufacture of the salts can be determined by studying the chemistry of their production at various temperatures in the system $CaO—P_2O_5—H_2O$. The composition of any calcium phosphate can be expressed through these components.

The object of this experiment is to determine (tentatively) the concentration of P_2O_5 in acid phosphorus solutions in conditions of unstable equilibrium at which the water-soluble calcium dihydrogen phosphate $Ca(H_2PO_4)_2 \cdot H_2O$ is stable at room temperature and an insoluble calcium hydrogen phosphate $CaHPO_4$ is stable at lower temperatures. The sought concentration of P_2O_5 corresponds to a

sharp change in the course of the curve illustrating the solubility of CaO in solutions of phosphoric acid. Six points should be found experimentally for the purpose.

This experiment should preferably be done by several students so that each student should determine one point. The graph should then be constructed using the experimental data of all students.

Procedure. Prepare six solutions* of phosphoric acid in six beakers. The solutions (100 g in each beaker) should contain 10, 19, 22, 25, 30, and 35% of P_2O_5. They should be prepared from a 40% solution (with respect to P_2O_5), density 1.38 g/cm^3.

Example of calculation: 10 g of P_2O_5 are required to prepare 100 g of 10% solution. This amount of P_2O_5 is contained in 25 g of 40% solution (the concentration is 4 times lower). The volume of the concentrated solution should be 25 : 1.38 = 18 ml. These 18 ml should be added, with stirring, to a beaker containing 75 ml of distilled water. (The amount of water needed to prepare 100 ml of 10% solution is 100 g — 25 g = 75 g $\approx$ 75 ml.)

Weigh out six portions of calcium oxide CaO each weighing 5.7 g. Place one beaker containing phosphoric acid into a cold water bath and add (*caution*!) CaO by small portions with stirring the mixture energetically to prepare a saturated (at room temperature) solution. Stop adding the salt when the dissolution of CaO discontinues. See to it that the temperature of solution does not rise above 20°C. To that end, change cold water at intervals. Allow the saturated solution to stand for 2-3 minutes and pour off the liquid phase.

The solution can turn cloudy after dissolution of the first portion of CaO, but it turns clear again after stirring for a few seconds. Cloudiness can be persistent in some saturated solutions. If this is the case, allow the solution to stand for 1-2 minutes during which the heavy particles settle down, and quickly pour off the cloudy solution.

Dissolve calcium oxide in all other solutions of phosphoric acid in the same way.

Place the beakers containing the undissolved calcium oxide into a drying cabinet and dry at 105-110°C to constant weight. Determine the weight of the precipitate in each beaker. Remember that the precipitate in the beaker with 10% P_2O_5 consists of $Ca(OH)_2$. Recalculate it with respect to CaO. Assume that CaO will not be hydrated in the other more concentrated solutions of phosphoric acid.

If only part of the weighed salt was dissolved to prepare a saturated solution, weigh the remainder. Calculate the quantity of CaO dissolved in 100 ml of each solution by subtracting the undissolved residue from the initial 5.7 g of CaO.

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* In order to save time, the solutions can be prepared beforehand by the laboratory assistant.

Recording the results and constructing the graph. Fill in the following table

Point No.	Composition of solution		Point No.	Composition of solution	
	% P_2O_5	% CaO		% P_2O_5	% CaO
1	10		4	25	
2	19		5	30	
3	22		6	35	

Plot % P_2O_5 against the axis of abscissas and % CaO against the axis of ordinates. Mark the six points by dots. Draw a solid line through the points corresponding to the concentrations of 10, 19 and 22% P_2O_5. Draw another line through the points with concentrations of 25, 30 and 35% P_2O_5. Find the point of their intersection. This will be the double point of $CaHPO_4 - Ca(H_2PO_4)_2 \cdot 2H_2O$. Draw a line perpendicular to the axis of abscissas from the point of intersection and determine the concentration of P_2O_5 at which the conversion occurs at room temperature.

At 25°C, the equilibrium in the system of these two salts exists at 24% of P_2O_5.

EXPERIMENT 69. CONSTRUCTING PHASE DIAGRAM OF THE SYSTEM NAPHTHALENE-PHENOL

Apparatus and reagents

Apparatus for determining the melting point. Naphthalene. Phenol.* Mixtures of naphthalene with phenol taken in the following ratios: 90:10; 80:20; 70:30; 60:40; 50:50; 40:60; 30:70; 20:80; and 10:90. Each mixture (1.2 g) should be obtained from the instructor in a separate test tube.

In order to construct a phase diagram, 11 points should be plotted. The work should therefore be conducted by several students. Each student finds his own point. The students assigned tasks 1 and 11 should determine the melting points of pure substances, phenol and naphthalene. The students assigned tasks 2 through 10 should determine the melting points and temperatures of crystallization of mixtures of phenol and naphthalene taken at known ratios.

* Diphenylamine can be used instead of phenol.

The apparatus used in this experiment is actually a wide (30-35 mm) test tube with a stopper provided with a thermometer and a wire stirrer.

Procedure. Obtain the apparatus for determining the melting point from the laboratory assistant. It should already contain the mixture of $C_{10}H_8$ and C_6H_5OH in the known ratio. Put the apparatus in a beaker containing water and fix in the stand so that it does not touch the beaker walls. Heat the beaker slowly until the mixture starts melting, and lower the flame of the burner so that the further rise of temperature should be 0.5° per minute. Stir the mixture carefully and observe the thermometer readings. The thermometer bulb should be in the middle of the test mixture. Raise the apparatus above the beaker and allow it to cool in air. Record the temperature at which first crystals begin precipitating.

Recording the results and constructing phase diagram. Put the results of your observations into your log-book and in the table on the blackboard:

Task No.	Composition of mixture, %		Melting point, °C	Crystallization point, °C
	Naphthalene	Phenol		
1	100	0		
2	90	10		
3	80	20		
4	70	30		
5	60	40		
6	50	50		
7	40	60		
8	30	70		
9	20	80		
10	10	90		
11	0	100		

Construct the phase diagram, plotting the composition of the system against the axis of abscissas and the melting points against the axis of ordinates. Using the graph, determine the percentage composition of the eutectic mixture and its melting point.

Appendix

TABLE 1. Atomic Weights and Numbers

Element	Symbol	At. No.	At. wt.
Aluminium	Al	13	26.981 54±1
Antimony	Sb	51	121.75±1
Argon	Ar	18	39.948±1
Arsenic	As	33	74.9216±1
Barium	Ba	56	137.33±1
Beryllium	Be	4	9.012 18±1
Bismuth	Bi	83	208.9804±1
Boron	B	5	10.811±5
Bromine	Br	35	79.904±1
Cadmium	Cd	48	112.41±1
Calcium	Ca	20	40.078±4
Carbon	C	6	12.011±1
Cerium	Ce	58	140.12±1
Cesium	Cs	55	132.9054±1
Chlorine	Cl	17	35.453±1
Chromium	Cr	24	51.9961±6
Cobalt	Co	27	58.9332±1
Copper	Cu	29	63.546±3
Dysprosium	Dy	66	162.50±3
Erbium	Er	68	167.26±3
Europium	Eu	63	151.96±1
Fluorine	F	9	18.998 403±1
Gadolinium	Gd	64	157.25±3
Gallium	Ga	31	69.723±4
Germanium	Ge	32	72.59±3
Gold	Au	79	196.9665±1
Hafnium	Hf	72	178.49±3
Helium	He	2	4.002 602±2
Hydrogen	H	1	1.007 94±7
Indium	In	49	114.82±1
Iodine	I	53	126.9045±1
Iridium	Ir	77	192.22±3
Iron	Fe	26	55.847±3
Krypton	Kr	36	83.80±1

Table 1 (continued)

Element	Symbol	At. No.	At. wt.
Lanthanum	La	57	138.9055±3
Lead	Pb	82	207.2±1
Lithium	Li	3	6.941±2
Lutetium	Lu	71	174.967±1
Magnesium	Mg	12	24.305±1
Manganese	Mn	25	54.9380±1
Mercury	Hg	80	200.59±3
Molybdenum	Mo	42	95.94±1
Neodymium	Nd	60	144.24±3
Neon	Ne	10	20.179±1
Nickel	Ni	28	58.69±1
Niobium	Nb	41	92.9064±1
Nitrogen	N	7	14.0067±1
Osmium	Os	76	190.2±1
Oxygen	O	8	15.9994±3
Palladium	Pd	46	106.42±1
Phosphorus	P	15	30.973 76±1
Platinum	Pt	78	195.08±3
Polonium	Po	84	208.9824
Potassium	K	19	39.0983±1
Praseodymium	Pr	59	140.9077±1
Radium	Ra	88	226.0254
Radon	Rn	86	222.0176
Rhenium	Re	75	186.207±1
Rhodium	Rh	45	102.9055±1
Rubidium	Rb	37	85.4678±3
Ruthenium	Ru	44	101.07±2
Samarium	Sm	62	150.36±3
Scandium	Sc	21	44.955 91±1
Selenium	Se	34	78.96±3
Silicon	Si	14	28.0855±3
Silver	Ag	47	107.8682±3
Sodium	Na	11	22.989 77±1
Strontium	Sr	38	87.62±1
Sulphur	S	16	32.066±6
Tantalum	Ta	73	180.9479±1
Technetium	Tc	43	97.9072
Tellurium	Te	52	127.60±3
Terbium	Tb	65	158.9254±1
Thallium	Tl	81	204.383±1
Thorium	Th	90	232.0381±1
Thulium	Tm	69	168.9342±1
Tin	Sn	50	118.710±7
Titanium	Ti	22	47.88±3
Tungsten	W	74	183.85±3
Uranium	U	92	238.0289±1
Vanadium	V	23	50.9415±1
Xenon	Xe	54	131.29±3
Ytterbium	Yb	70	173.04±3

Table 1 (concluded)

Element	Symbol	At. No.	At. wt.
Yttrium	Y	39	88.9059±1
Zinc	Zn	30	65.39±2
Zirconium	Zr	40	91.224±2

Note. 1. Atomic weights are based on carbon-12; its 1/12th fraction is assumed as a unit of atomic weight.
2. Atomic weights are given according to the International Table of Atomic Weights, 1983; the accuracy is given to the last significant decimal.

TABLE 2. Saturated Vapour Pressure at Equilibrium with Water

Temperature, °C	Vapour pressure, mm Hg	Temperature, °C	Vapour pressure, mm Hg
0	4.58	19	16.48
5	6.54	20	17.53
10	9.20	21	18.65
15	12.79	22	19.82
16	13.63	23	21.09
17	14.53	24	22.37
18	15.47	25	23.75

TABLE 3. Standard Enthalpy of Formation of Some Substances at 760 mm Hg and 298 K

Substance	ΔH°_{298}	
	kJ/mol	kcal/mol
CH_4 (g)	—74.9	—17.9
C_2H_2 (g)	+226.8	+54.2
CO (g)	—110.5	—26.4
CO_2 (g)	—393.3	—94.0
CaO (c)	—635.5	—151.9
$CaCO_3$ (c)	—1205.0	—288.0
$Ca(FeO_2)_2$ (c)	—1665.2	—398.0
Cu_2O (c)	—166.5	—39.8
Cu_2S (c)	—82.0	—19.6
Fe_2O_3 (c)	—822.1	—196.5
H_2O (g)	—241.8	—57.8
H_2O (l)	—285.8	—68.3
HCl (g)	—91.6	—21.9

Table 3 (concluded)

Substance	ΔH°_{298}	
	kJ/mol	kcal/mol
H_2S (g)	—20.9	—5.0
MgO (c)	—601.6	—143.8
NH_3 (g)	—46.0	—11.0
NO (g)	+90.3	+21.6
NO_2 (g)	+33.9	+8.1
N_2O_4 (g)	+9.2	+2.2
ZnO (c)	—350.7	—83.9

TABLE 4. Density of Aqueous Solutions of Some Acids, Alkalies and Ammonia at 20°C (g/ml)

Concentrations, % \ Substance	H_2SO_4	HNO_3	HCl	KOH	NaOH	NH_3
2	1.013	1.011	1.009	1.016	1.023	0.992
4	1.027	1.022	1.019	1.033	1.046	0.983
6	1.040	1.033	1.029	1.048	1.069	0.973
8	1.055	1.044	1.039	1.065	1.092	0.967
10	1.069	1.056	1.049	1.082	1.115	0.960
12	1.083	1.068	1.059	1.100	1.137	0.953
14	1.098	1.080	1.069	1.118	1.159	0.946
16	1.112	1.093	1.079	1.137	1.181	0.939
18	1.127	1.106	1.083	1.156	1.213	0.932
20	1.143	1.119	1.100	1.176	1.225	0.926
22	1.158	1.132	1.110	1.196	1.247	0.919
24	1.174	1.145	1.121	1.217	1.268	0.913
26	1.190	1.158	1.132	1.240	1.289	0.908
28	1.205	1.171	1.142	1.263	1.310	0.903
30	1.224	1.184	1.152	1.286	1.332	0.898
32	1.238	1.198	1.163	1.310	1.352	0.893
34	1.255	1.211	1.173	1.334	1.374	0.889
36	1.273	1.225	1.183	1.358	1.395	0.884
38	1.290	1.238	1.194	1.384	1.416	
40	1.307	1.251		1.411	1.437	
42	1.324	1.264		1.437	1.458	
44	1.342	1.277		1.460	1.478	
46	1.361	1.290		1.485	1.499	
48	1.380	1.303		1.511	1.519	
50	1.399	1.316		1.538	1.540	
52	1.419	1.328		1.564	1.560	
54	1.439	1.340		1.590	1.580	
56	1.460	1.351		1.616	1.601	
58	1.482	1.362			1.622	

Table 4 (concluded)

Concentration, % \ Substance	H_2SO_4	HNO_3	HCl	KOH	NaOH	NH_3
60	1.503	1.373			1.643	
62	1.525	1.384				
64	1.547	1.394				
66	1.571	1.403				
68	1.594	1.412				
70	1.617	1.421				
72	1.640	1.429				
74	1.664	1.437				
76	1.687	1.445				
78	1.710	1.453				
80	1.732	1.460				
82	1.755	1.467				
84	1.776	1.474				
88	1.808	1.486				
90	1.819	1.491				
92	1.830	1.496				
94	1.837	1.500				
98	1.841	1.510				
100	1.838	1.522				

TABLE 5. Solubility of NaCl and $K_2Cr_2O_7$ (in g/100 ml H_2O)

Substance	Temperature, °C										
	0	10	20	30	40	50	60	70	80	90	100
NaCl	35.7	35.8	36.0	36.6	36.6	37.0	37.3	37.8	38.4	39.0	39.8
$K_2Cr_2O_7$	4.6	8.1	12.5	18.2	26.0	35.0	45.3	56.2	41.1	83.2	102.0

TABLE 6. Dissociation Degree of Some Acids, Bases and Salts in Aqueous Solutions* (0.1 *N*) at 18 °C

Acid	Dissociation degree, %	Base or Salt	Dissociation degree, %
HNO_3	92	KOH	89
HCl	91	NaOH	84
HBr	90	$NH_3 \cdot H_2O$	1.3
HI	90		

Table 6 (concluded)

Acid	Dissociation degree, %	Base or Salt	Dissociation degree, %
H_2SO_4	58	Me^+A^- (KCl)	83
H_3PO_4	36	$Me_2^+A^{2-}$ (K_2SO_4) or	
$SO_2 \cdot H_2O$	20	$Me^{2+}A_2^-$ ($BaCl_2$)	75
CH_3COOH	1.3	$Me_3^+A^{3-}$ (K_3PO_4) or	
H_2CO_3	0.17	$Me^{3+}A_3^-$ ($AlCl_3$)	65
H_2S	0.07	$Me^{2+}A^{2-}$ ($CuSO_4$)	40
H_3BO_3	0.01		
HCN	0.007		

* Apparent dissociation degrees are given for strong electrolytes. First dissociation degrees are given for polybasic acids.

TABLE 7. Dissociation Constants for Water and Some Weak Acids and Bases in Aqueous Solutions at 18-25°C

Compound	Dissociation step	K
H_2O		1.8×10^{-16}
HNO_2		4.6×10^{-4}
ortho-H_3BO_3	I	5.3×10^{-10}
	II	1.8×10^{-13}
	III	1.6×10^{-14}
tetra-$H_2B_4O_7$	I	$\approx 10^{-4}$
	II	$\approx 10^{-9}$
meta-H_2SiO_3	I	2×10^{-10}
H_2O_2		2.4×10^{-12}
$SO_2 \cdot H_2O$	I	1.6×10^{-2}
	II	6.3×10^{-8}
H_2S	I	6×10^{-8}
	II	1×10^{-14}
H_2CO_3	I	4.4×10^{-7}
	II	4.7×10^{-11}
ortho-H_3PO_4	I	7.5×10^{-3}
	II	6.3×10^{-8}
	III	2.2×10^{-12}
HClO		3.2×10^{-8}
H_2CrO_4	I	1.8×10^{-1}
	II	3.2×10^{-7}
HCN		7.9×10^{-10}
CH_3COOH		1.8×10^{-5}
$Al(OH)_3$	III	1.4×10^{-11}
$NH_3 \cdot H_2O$		1.8×10^{-5}
$Cd(OH)_2$	II	5×10^{-3}

TABLE 8. Solubility Products of Sparingly Soluble Substances (at 18-25 °C)

Substance	SP	Substance	SP
AgBr	6×10^{-13}	FeS	5×10^{-18}
AgCN	7×10^{-15}	Hg_2Cl_2	1.3×10^{-18}
Ag_2S	6×10^{-50}	$MgCO_3$	1.0×10^{-5}
AgSCN	1.1×10^{-12}	$Mg(OH)_2$	2×10^{-11}
AgCl	1.8×10^{-10}	MgS	2×10^{-15}
Ag_2CO_3	8.2×10^{-12}	$Mn(OH)_2$	2×10^{-13}
Ag_2CrO_4	4×10^{-12}	MnS	2.5×10^{-10}
AgI	1.1×10^{-16}	$NiCO_3$	1.3×10^{-7}
$BaCO_3$	5×10^{-9}	$Ni(OH)_2$	10^{-15}–10^{-18}
$BaC_2O_4 \cdot 2H_2O$	1.1×10^{-7}	$PbCO_3$	7.5×10^{-14}
$BaCrO_4$	1.6×10^{-12}	$PbCl_2$	2×10^{-5}
$BaSO_4$	1.1×10^{-10}	$PbCrO_4$	1.8×10^{-14}
$CaCO_3$	5×10^{-9}	PbI_2	8×10^{-9}
$CaC_2O_4 \cdot H_2O$	2×10^{-9}	$Pb(OH)_2$	2×10^{-16}
$CaSO_4 \cdot 2H_2O$	1×10^{-5}	PbS	1×10^{-27}
CdS	1×10^{-29}	$PbSO_4$	1.6×10^{-8}
$Co(OH)_2$	2×10^{-15}	Sb_2S_3	1×10^{-30}
CuC_2O_4	2.5×10^{-22}	SnS	1×10^{-26}
Cu_2S	1×10^{-48}	$SrCO_3$	1.1×10^{-10}
CuS	6×10^{-36}	$SrC_2O_4 \cdot H_2O$	5.6×10^{-8}
$FeCO_3$	2.5×10^{-11}	$SrSO_4$	3.2×10^{-7}
$Fe(OH)_2$	1×10^{-15}	$Zn(OH)_2$	1×10^{-17}
Fe(OOH)	3.8×10^{-38}	ZnS	1.6×10^{-24}

TABLE 9. pH Range of Some Indicators

Indicator	pH range	Colour change
Thymol blue	1.2-2.8	from red to yellow*
Methyl orange	3.1-4.4	from red to orange yellow
Methyl red	4.4-6.2	from red to yellow
Litmus	5.0-8.0	from red to blue
Thymol blue	8.0-9.6	from yellow to blue*
Phenolphthalein	8.2-10.0	from colourless to crimson
Alizarin yellow	10.1-12.1	from yellow to lilac violet
Tropeolin 0	11.0-13.0	from yellow to orange brown
Indigo carmine	12.0-14.0	from blue to yellow

* The indicator thymol blue has two pH ranges: at pH $\leqslant$ 1.2 its colour is red; as the pH increases to 2.8 it turns yellow and remains so to pH=8. During further increase of pH, the colour of the solution changes to blue and remains so at pH $\geqslant$ 9.6.

TABLE 10. Hydrolysis of Salts (in 0.1 *M* Solutions at 25°C)

Salt	Degree of hydrolysis, in %	Salt	Degree of hydrolysis, in %
NH_4Cl	0.007	NaH_2PO_4	0.0004
CH_3COONH_4	0.5	Na_2CO_3	4.0
$(NH_4)_2S$	99.0	$NaHCO_3$	0.005
NH_4HS	7.0	Na_2S	99.0
$Na_2B_4O_7$	0.5	NaHS	0.10
Na_2SO_3	0.13	NaClO	0.18
$NaHSO_3$	0.0002	KCN	1.2
CH_3COONa	0.007	$Al_2(SO_4)_3$	3.5
Na_3PO_4	34	$Al(CH_3COO)_3$	40.0
Na_2HPO_4	0.13	$Fe(CH_3COO)_3$	32.0

TABLE 11. Standard Electrode Potentials of Some Oxidation-reduction Systems

Oxidized form	Reduced form	Electrode process	φ°, V
		Aluminium	
Al^{3+}	Al (c)	$Al^{3+} + 3e^- = Al$	−1.66
		Arsenic	
AsO_4^{3-}	AsO_2^-	$AsO_4^{3-} + 2e^- + 2H_2O = AsO_2^- + 4OH^-$	−0.67
AsO_4^{3-}	As (c)	$AsO_4^{3-} + 5e^- + 8H^+ = As + 4H_2O$	+0.65
		Barium	
Ba^{2+}	Ba (c)	$Ba^{2+} + 2e^- = Ba$	−2.90
		Bismuth	
BiO_3^-	Bi^{3+}	$BiO_3^- + 2e^- + 6H^+ = Bi^{3+} + 3H_2O$	+1.80
		Bromine	
BrO_3^-	Br_2 (l)	$2BrO_3^- + 10e^- + 6H_2O = Br_2 + 12OH^-$	+0.50
BrO_3^-	Br^-	$BrO_3^- + 6e^- + 3H_2O = Br^- + 6OH^-$	+0.61
Br_2 (l)	$2Br^-$	$Br_2 + 2e^- = 2Br^-$	+1.07
HBrO	Br^-	$HBrO + 2e^- + H^+ = Br^- + H_2O$	+1.34
BrO_3^-	Br^-	$BrO_3^- + 6e^- + 6H^+ = Br^- + 3H_2O$	+1.44
$2BrO_3^-$	Br_2 (l)	$2BrO_3^- + 10e^- + 12H^+ = Br_2 + 6H_2O$	+1.52
		Cadmium	
Cd^{2+}	Cd (c)	$Cd^{2+} + 2e^- = Cd$	−0.40

Table 11 (continued)

Oxidized form	Reduced form	Electrode process	φ°, V
		Calcium	
Ca^{2+}	Ca (c)	$Ca^{2+} + 2e^- = Ca$	−2.87
		Chlorine	
ClO_4^-	Cl^-	$ClO_4^- + 8e^- + 4H_2O = Cl^- + 8OH^-$	+0.56
Cl_2 (g)	$2Cl^-$	$Cl_2 + 2e^- = 2Cl^-$	+1.36
ClO_4^-	Cl^-	$ClO_4^- + 8e^- + 8H^+ = Cl^- + 4H_2O$	+1.38
ClO_3^-	Cl^-	$ClO_3^- + 6e^- + 6H^+ = Cl^- + 3H_2O$	+1.45
ClO_3^-	Cl_2 (g)	$2ClO_3^- + 10e^- + 12H^+ = Cl_2 + 6H_2O$	+1.47
HClO	Cl^-	$HClO + 2e^- + H^+ = Cl^- + H_2O$	+1.50
		Chromium	
Cr^{3+}	Cr (c)	$Cr^{3+} + 3e^- = Cr$	−0.74
$Cr_2O_7^{2-}$	$2Cr^{3+}$	$Cr_2O_7^{2-} + 6e^- + 14H^+ = 2Cr^{3+} + 7H_2O$	+1.33
		Cobalt	
Co^{2+}	Co (c)	$Co^{2+} + 2e^- = Co$	−0.28
CoOOH	$Co(OH)_2$	$CoOOH + e^- + H_2O = Co(OH)_2 + OH^-$	+0.17
Co^{3+}	Co (c)	$Co^{3+} + 3e^- = Co$	+0.33
Co^{3+}	Co^{2+}	$Co^{3+} + e^- = Co^{2+}$	+1.81
		Copper	
CuS	Cu	$CuS + 2e^- = Cu + S^{2-}$	−0.71
Cu^{2+}	Cu (c)	$Cu^{2+} + 2e^- = Cu$	+0.34
		Fluorine	
F_2 (g)	$2F^-$	$F_2 + 2e^- = 2F^-$	+2.87
		Gold	
Au^{3+}	Au (c)	$Au^{3+} + 3e^- = Au$	+1.50
		Hydrogen	
H_2O	H_2	$2H_2O + 2e^- = H_2 + 2OH^-$	−0.83
$2H^+$	H_2 (g)	$2H^+ + 2e^- = H_2$	−0.00
		Iodine	
IO_3^-	I^-	$IO_3^- + 6e^- + 3H_2O = I^- + 6OH^-$	+0.25
I_2	$2I^-$	$I_2 + 2e^- = 2I^-$	+0.54
IO_3^-	I^-	$IO_3^- + 6e^- + 6H^+ = I^- + 3H_2O$	+1.09
$2IO_3^-$	I_2	$2IO_3^- + 10e^- + 12H^+ = I_2 + 6H_2O$	+1.19
		Iron	
FeOOH	$Fe(OH)_2$	$FeOOH + e^- + H_2O = Fe(OH)_2 + OH^-$	−0.56
Fe^{2+}	Fe (c)	$Fe^{2+} + 2e^- = Fe$	−0.44

Table 11 (continued)

Oxidized form	Reduced form	Electrode process	φ°, V
Fe^{3+}	Fe^{2+}	$Fe^{3+} + e^- = Fe^{2+}$	+0.77
		Lead	
Pb^{2+}	Pb (c)	$Pb^{2+} + 2e^- = Pb$	−0.13
PbO_2 (c)	Pb^{2+}	$PbO_2 + 2e^- + 4H^+ = Pb^{2+} + 2H_2O$	+1.45
		Lithium	
Li^+	Li (c)	$Li^+ + e^- = Li$	−3.04
		Magnesium	
Mg^{2+}	Mg (c)	$Mg^{2+} + 2e^- = Mg$	−2.36
		Manganese	
Mn^{2+}	Mn (c)	$Mn^{2+} + 2e^- = Mn$	−1.18
MnO_4^{2-}	MnO_2 (c)	$MnO_4^{2-} + 2H_2O + 2e^- = MnO_2 + 4OH^-$	+0.51
MnO_4^-	MnO_4^{2-}	$MnO_4^- + e^- = MnO_4^{2-}$	+0.56
MnO_4^-	MnO_2 (c)	$MnO_4^- + 3e^- + 2H_2O = MnO_2 + 4OH^-$	+0.60
MnO_2 (c)	Mn^{2+}	$MnO_2 + 2e^- + 4H^+ = Mn^{2+} + 2H_2O$	+1.23
MnO_4^-	Mn^{2+}	$MnO_4^- + 5e^- + 8H^+ = Mn^{2+} + 4H_2O$	+1.52
MnO_4^-	MnO_2 (c)	$MnO_4^- + 3e^- + 4H^+ = MnO_2 + 2H_2O$	+1.69
		Mercury	
Hg_2Cl_2	2Hg (l)	$Hg_2Cl_2 + 2e^- = 2Hg + 2Cl^-$	+0.27
Hg_2^{2+}	2Hg (l)	$Hg_2^{2+} + 2e^- = 2Hg$	+0.80
Hg^{2+}	Hg (l)	$Hg^{2+} + 2e^- = Hg$	+0.85
$2Hg^{2+}$	Hg_2^{2+}	$2Hg^{2+} + 2e^- = Hg_2^{2+}$	+0.92
		Nickel	
Ni^{2+}	Ni (c)	$Ni^{2+} + 2e^- = Ni$	−0.25
NiOOH	$Ni(OH)_2$	$NiOOH + e^- + H_2O = Ni(OH)_2 + OH^-$	+0.49
		Nitrogen	
NO_3^-	NO_2 (g)	$NO_3^- + e^- + H_2O = NO_2 + 2OH^-$	−0.85
N_2	$NH_3 \cdot H_2O$	$N_2 + 2e^- + 4H_2O = 2NH_3 \cdot H_2O$	−0.74
NO_2^-	$NH_3 \cdot H_2O$	$NO_2^- + 6e^- + 6H_2O = NH_3 \cdot H_2O + 7OH^-$	−0.15
NO_3^-	NO (g)	$NO_3^- + 3e^- + 2H_2O = NO + 4OH^-$	−0.14
NO_3^-	NO_2^-	$NO_3^- + 2e^- + H_2O = 2OH^- + NO_2^-$	+0.01
N_2 (g)	$2NH_4^+$	$N_2 + 6e^- + 8H^+ = 2NH_2^+$	+0.27
NO_3^-	NO_2 (g)	$NO_3^- + e^- + 2H^+ = NO_2 + H_2O$	+0.78
NO_3^-	NH_4^+	$NO_3^- + 3e^- + 10H^+ = NH_4^+ + 3H_2O$	+0.87
NO_3^-	NO (g)	$NO_3^- + 3e^- + 4H^+ = NO + 2H_2O$	+0.96
HNO_2	NO (g)	$HNO_2 + e^- + H^+ = NO\ (g) + H_2O$	+1.00

Table 11 (continued)

Oxidized form	Reduced form	Electrode process	φ°, V
		Oxygen	
O_2 (g)	$2OH^-$	$O_2 + 4e^- + 2H_2O = 4OH^-$	+0.40
O_2 (g)	H_2O_2	$O_2 + 2e^- + 2H^+ = H_2O_2$	+0.68
O_2 (g)	$2H_2O$	O_2 (g) $+ 4e^- + 4H^+ = 2H_2O$	+1.23
H_2O_2	H_2O	$H_2O_2 + 2e^- + 2H^+ = 2H_2O$	+1.78
		Phosphorus	
H_3PO_4	P (c)	$H_3PO_4 + 5e^- + 5H^+ = P + 4H_2O$	−0.41
		Potassium	
K^+	K (c)	$K^+ + e^- = K$	−2.92
		Silver	
AgCl (c)	Ag (c)	$AgCl + e^- = Ag + Cl^-$	+0.22
$Ag(NH_3)_2^+$	Ag (c)	$Ag(NH_3)_2^+ + e^- = Ag + 2NH_3$	+0.37
Ag^+	Ag (c)	$Ag^+ + e^- = Ag$	+0.80
		Sodium	
Na^+	Na (c)	$Na^+ + e^- = Na$	−2.71
		Sulphur	
SO_4^{2-}	SO_3^{2-}	$SO_4^{2-} + 2e^- + H_2O = SO_3^{2-} + 2OH^-$	−0.93
SO_3^{2-}	S (c)	$SO_3^{2-} + 4e^- + 3H_2O = S + 6OH^-$	−0.90
$2SO_3^{2-}$	$S_2O_3^{2-}$	$2SO_3^{2-} + 3H_2O + 4e^- = S_2O_3^{2-} + 6OH^-$	−0.58
S (c)	H_2S (g)	$S + 2e^- + 2H^+ = H_2S$	+0.17
SO_4^{2-}	$SO_2 \cdot H_2O$	$SO_4^{2-} + 2e^- + 4H^+ = SO_2 \cdot H_2O + H_2O$	+0.17
SO_4^{2-}	H_2S (g)	$SO_4^{2-} + 8e^- + 10H^+ = H_2S + H_2O$	+0.31
SO_4^{2-}	S (c)	$SO_4^{2-} + 6e^- + 8H^+ = S + 4H_2O$	+0.36
$SO_2 \cdot H_2O$	S (c)	$SO_2 \cdot H_2O + 4e^- + 4H^+ = S + 3H_2O$	+0.45
$S_2O_8^{2-}$	$2SO_4^{2-}$	$S_2O_8^{2-} + 2e^- = 2SO_4^{2-}$	+2.01
		Strontium	
Sr^{2+}	Sr (c)	$Sr^{2+} + 2e^- = Sr$	−2.89
		Tin	
Sn^{2+}	Sn (c)	$Sn^{2+} + 2e^- = Sn$	−0.14
Sn^{4+}	Sn^{2+}	$Sn^{4+} + 2e^- = Sn^{2+}$	+0.15
		Titanium	
Ti^{3+}	Ti (c)	$Ti^{3+} + 3e^- = Ti$	−1.23
TiO^{2+}	Ti (c)	$TiO^{2+} + 4e^- + 2H^+ = Ti + H_2O$	−0.88
TiO^{2+}	Ti^{3+}	$TiO^{2+} + e^- + 2H^+ = Ti^{3+} + H_2O$	+0.10

Table 11 (concluded)

Oxidized form	Reduced form	Electrode process	φ°, V
		Tungsten	
WO_4^{2-}	W (c)	$WO_4^{2-} + 6e^- + 4H_2O = W + 8OH^-$	−1.10
WO_4^{2-}	W (c)	$WO_4^{2-} + 6e^- + 8H^+ = W + 4H_2O$	+0.05
		Vanadium	
V^{2+}	V (c)	$V^{2+} + 2e^- = V$	−1.17
V^{3+}	V^{2+}	$V^{3+} + e^- = V^{2+}$	−0.26
VO^{2+}	V^{3+}	$VO^{2+} + e^- + 2H^+ = V^{3+} + H_2O$	+0.34
VO_2^+	V^{2+}	$VO_2^+ + 3e^- + 4H^+ = 2H_2O + V^{2+}$	+0.36
VO_2^+	V^{3+}	$VO_2^+ + 2e^- + 4H^+ = V^{3+} + 2H_2O$	+0.66
VO_2^+	VO^{2+}	$VO_2^+ + e^- + 2H^+ = VO^{2+} + H_2O$	+1.00
		Zinc	
Zn^{2+}	Zn (c)	$Zn^{2+} + 2e^- = Zn$	−0.76

TABLE 12. Instability Constants of Some Complex Ions

Complex ion	K_{inst}	Complex ion	K_{inst}
$[Ag(CN)_2]^-$	1×10^{-21}	$[Fe(CN)_6]^{4-}$	1×10^{-37}
$[Ag(NH_3)_2]^+$	7×10^{-8}	$[Fe(CN)_6]^{3-}$	1×10^{-44}
$[Ag(S_2O_3)_2]^{3-}$	1×10^{-13}	$[Fe(SCN)]^{2+}$	1×10^{-3}
$[CdCl_4]^{2-}$	9×10^{-3}	$[HgBr_4]^{2-}$	1×10^{-21}
$[CdI_4]^{2-}$	8×10^{-7}	$[HgCl_4]^{2-}$	8×10^{-16}
$[Cd(CN)_4]^{2-}$	1×10^{-17}	$[HgI_4]^{2-}$	1×10^{-30}
$[Cd(NH_3)_4]^{2+}$	8×10^{-8}	$[Hg(SCN)_4]^{2-}$	1×10^{-22}
$[Cd(NH_3)_6]^{2+}$	8×10^{-6}	$[Ni(CN)_4]^{2-}$	3×10^{-16}
$[Co(NH_3)_6]^{3+}$	6×10^{-36}	$[Ni(NH_3)_6]^{2+}$	2×10^{-9}
$[Cu(NH_3)_4]^{2+}$	2×10^{-13}	$[Zn(CN)_4]^{2-}$	2×10^{-17}
$[Cu(CN)_4]^{3-}$	5×10^{-28}	$[Zn(NH_3)_4]^{2+}$	4×10^{-10}

TABLE 13. Solubility of Some Salts and Bases in Water

Anion	Cation																		
	Li^+	Na^+	K^+	NH_4^+	Cu^{2+}	Ag^+	Mg^{2+}	Ca^{2+}	Sr^{2+}	Ba^{2+}	Zn^{2+}	Hg^{2+}	Al^{3+}	Sn^{2+}	Pb^{2+}	Bi^{3+}	Mn^{2+}	Fe^{3+}	Fe^{2+}
Cl^-	S	S	S	S	S	I	S	S	S	S	S	S	S	S	SS	—	S	S	S
Br^-	S	S	S	S	S	I	S	S	S	S	S	SS	S	S	SS	—	S	S	S
I^-	S	S	S	S	—	I	S	S	S	S	S	I	S	S	I	—	I	—	S
NO_3^-	S	S	S	S	S	S	S	S	S	S	S	S	S	—	S	S	S	S	S
CH_3COO^-	S	S	S	S	S	S	S	S	S	S	S	S	S	—	S	—	S	—	S
S^{2-}	S	S	S	S	I	I	—	S	S	S	I	I	—	I	I	I	I	I	I
SO_3^{2-}	S	S	S	S	I	I	I	I	I	I	I	I	—	—	I	I	I	—	I
SO_4^{2-}	S	S	S	S	S	SS	S	SS	I	I	S	—	S	S	I	—	S	S	S
CO_3^{2-}	S	S	S	S	—	I	I	I	I	I	I	—	—	—	I	I	I	—	I
SiO_3^{2-}	S	S	S	—	—	—	I	I	I	I	I	—	I	—	I	—	I	I	I
CrO_4^{2-}	S	S	S	S	I	I	S	SS	SS	I	I	I	—	—	I	I	I	—	—
PO_4^{3-}	I	S	S	S	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I
OH^-	S	S	S	S	I	—	I	SS	SS	S	I	—	I	I	I	I	I	I	I

Note: "S" stands for soluble, "I" for insoluble, "SS" for slightly soluble, and dash (—) indicates that the substance does not exist or is decomposed in aqueous solution.

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